I.C.P analytical techniques applied to the hydrogeochemistry of the southern Lincolnshire Limestone aquifer

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by

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ABSTRACT

The hydrogeochemistry of the southern Lincolnshire Limestone is investigated employing inductively coupled plasma - optical emission spectrometry (ICP-OES) as the primary analytical technique. Two simultaneous, multi-element instruments were used. The principles of the technique and comparisons of the hardware, operating conditions and routine sample preparation methods are outlined and realistic levels of precision and detection limits evaluated. The range of determinations in the groundwaters was extended by the development of novel sample treatment techniques including the determination of dissolved sulphide down to the 1 $\mu g\ l^{-1}$ level using a gas-liquid separator, and the determination of rare earth elements in groundwater evaporation residues.

The methods were applied to the analysis of groundwaters and rocks of the Lincolnshire Limestone in southern Lincolnshire. The geology, hydrogeology and hydrochemistry of the aquifer are reviewed and the sample collection methods described, stressing the precautions taken to avoid contamination.

The Lincolnshire Limestone is an aquifer of considerable heterogeneity, argillaceous limestones are intercalated with pure oolites and it is confined by predominantly clastic formations. The major element chemistry of the groundwaters follow a down-dip trend between calcium-bicarbonate-sulphate waters near outcrop and saline, non-potable waters in the east. The groundwaters are sub-divided into zones based on the processes of calcite dissolution, ion exchange and the mixing of recharge and saline interstitial waters. Minor and trace element behaviour is controlled by a combination of oxidation-reduction reactions, adsorption on clay minerals and organic matter, mineral solubilities, complex formation and

groundwater pH. Ultimately the low levels of most trace metals are limited by their low abundance in the limestone.

Temporal hydrochemical trends are identified, and the influence of man, with reference to the down-gradient migration of agrichemical pollutants (e.g. nitrates) is assessed. Fluctuations in the movement of the potable/saline water interface are noted and theories on the origin of the saline waters reviewed.

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Being a CASE student, finding temporary accomodation proved difficult at times and I am grateful to those who provided short-term solutions, notably Sue Bryant in Wallingford and Addis, Karen and Co. in London.

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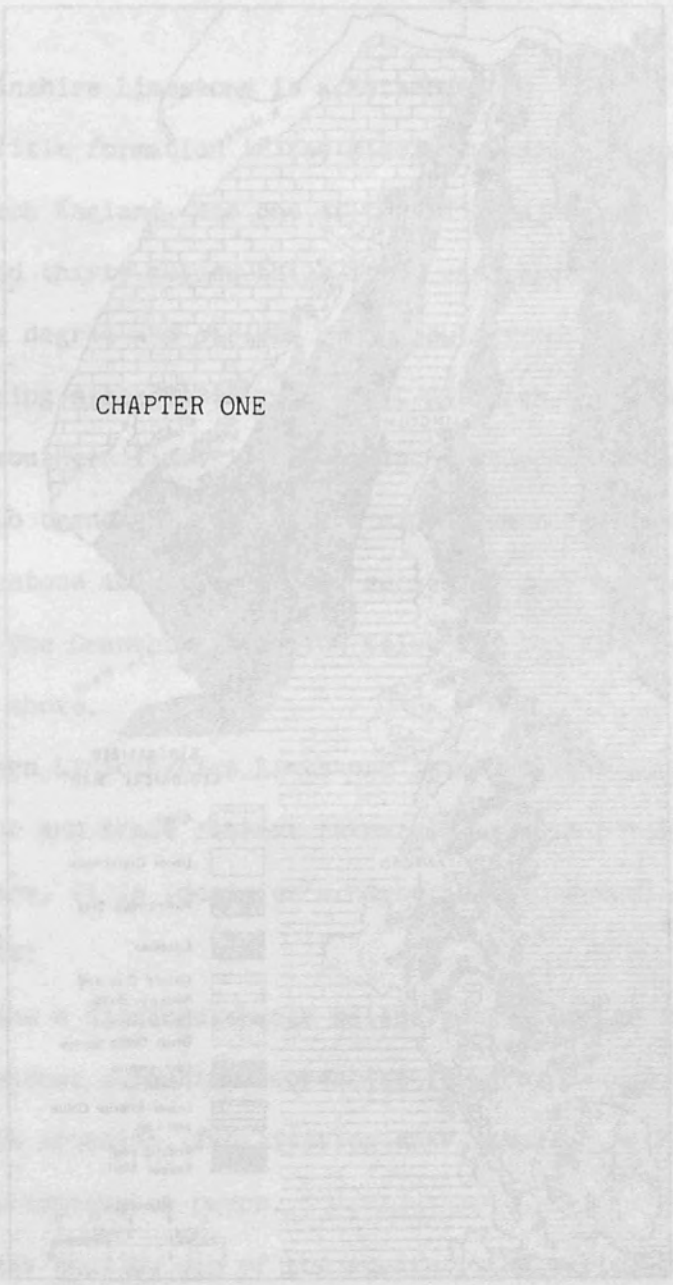


CHAPTER ONE

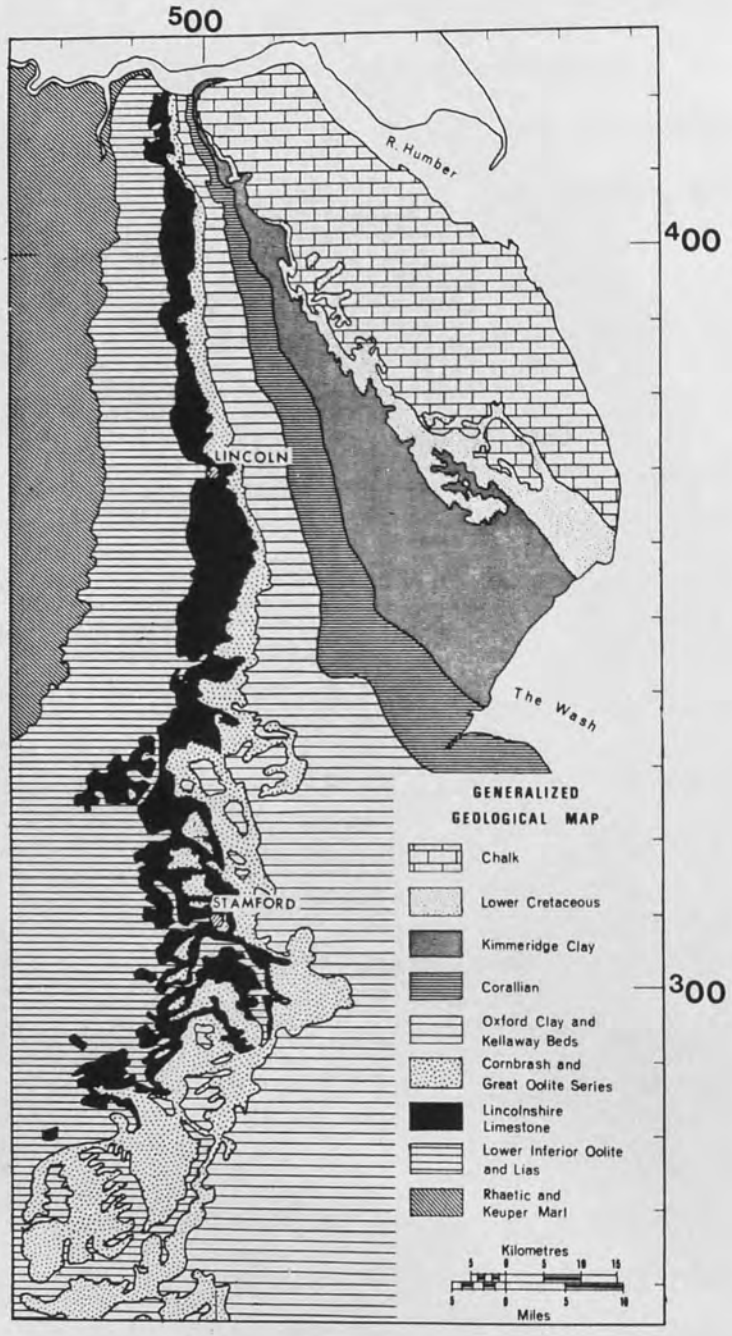


Figure 1.1

Generalised geological map of Lincolnshire and adjoining counties showing the outcrop of the Lincolnshire Limestone (after Downing and Williams, 1969).

1. THE LINCOLNSHIRE LIMESTONE AQUIFER: AN OVERVIEW

1.1 INTRODUCTION

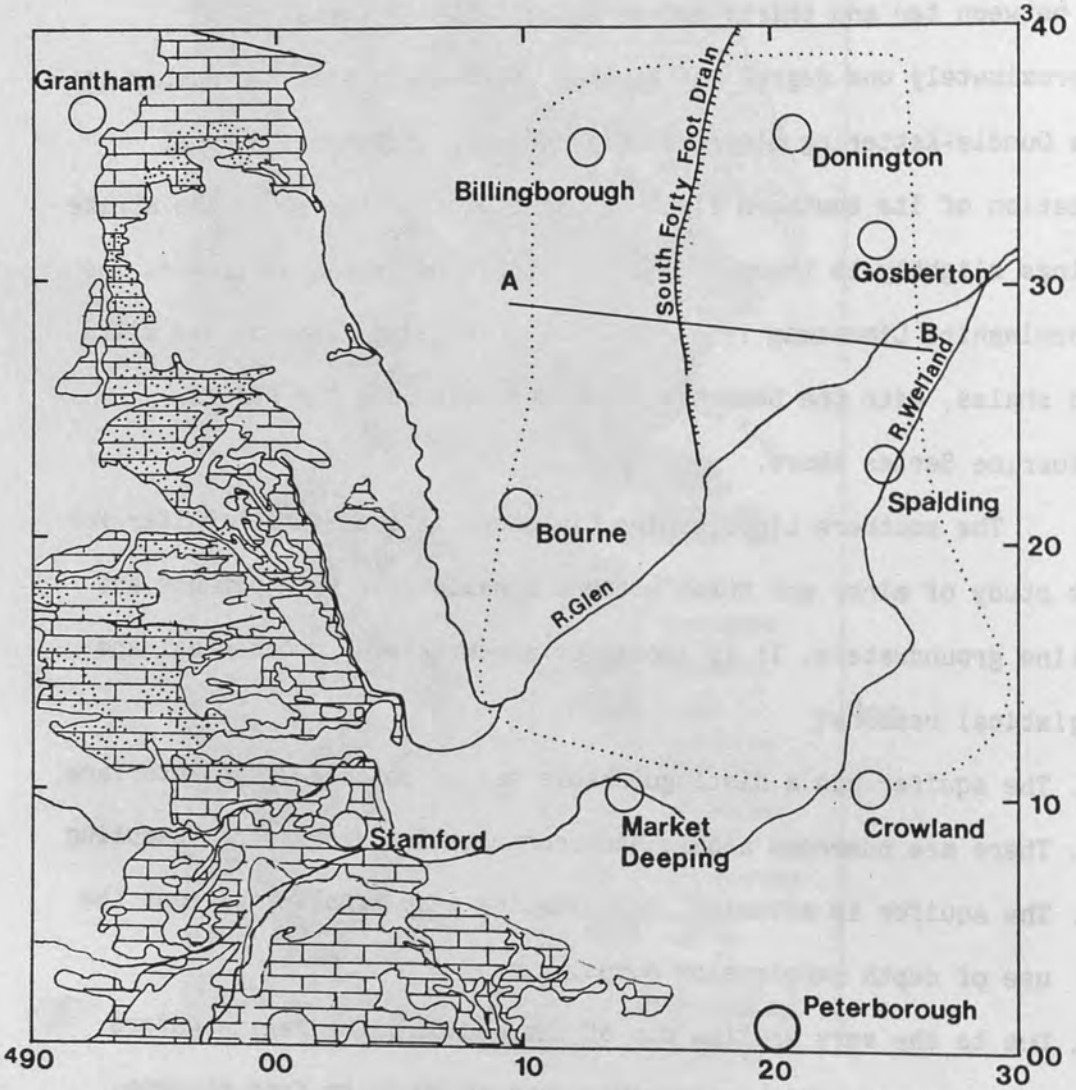
The Lincolnshire Limestone is a heterogenous, but predominantly oolitic formation in the Middle Jurassic (Bajocian) sequence of Eastern England, and one of the UK's major aquifers. It is between ten and thirty metres thick, dips eastwards at approximately one degree and strikes north-south from the Humber to the Oundle-Kettering district (figure 1.1), although the exact location of its southern limit is uncertain. In the south the strike swings slightly to trend NNE-SSW and the dip becomes shallower. The Lincolnshire Limestone is confined by a series of impermeable silts and shales, with the Grantham Formation below and the Upper Estuarine Series above.

The southern Lincolnshire Limestone is a suitable aquifer for the study of minor and trace element behaviour in both potable and saline groundwaters. It is ideal for a number of hydrochemical and logistical reasons:

1. The aquifer has a distinguishable saline/potable water interface
2. There are numerous accessible boreholes for groundwater sampling
3. The aquifer is artesian, facilitating easy sampling without the use of depth samplers or pumps.
4. Due to the very shallow dip of the aquifer, the saline waters downdip are readily accessible even at 30-40 km from outcrop.
5. The BGS had previous experience in the area, and had already developed good working links with Anglian Water (AW)
6. A considerable amount of geological and hydrogeological literature exists for the aquifer
7. Research projects on the Lincolnshire Limestone were in progress at other institutions, including those of D. Emery (Cambridge

Figure 1.2

Map showing the location of the sampling area (enclosed by a dotted line) in relation to the outcrop of the Lincolnshire Limestone (shaded). Stippling marks the approximate area of boulder clay cover. Line A-B defines the line of section used in figure 1.3.



University), studying the diagenesis of the Lincolnshire Limestone and P. Bishop (Birmingham University) collecting carbon isotope data for the groundwaters of the middle and southern part of the aquifer

8. Rock core was available for analysis via BGS and D. Emery.

The flat fenland between Bourne and Spalding (figure 1.2) is dissected by numerous man-made dykes and tributaries of the rivers Glen and Welland, which drain into the Wash. Upper Jurassic clays underlie much of this area, but are obscured by a thick mantle of glacial and fenland deposits. The rich soils are intensively farmed and most of the groundwater abstracted from private boreholes is for agricultural use. The population is generally sparse, being concentrated in the towns of Bourne, Spalding and Market Deeping. The sole economic application of the geology of the area, is the working of glacial and fluvial sand and gravels around Baston, in the south-east. However, the Lincolnshire Limestone has been extensively quarried for building stone and road aggregate along its outcrop.

1.2 GEOLOGY

Details of the geology of the Lincolnshire Limestone have been reported extensively in the literature from the early Geological Survey memoirs (Skertchley, 1877; Jukes-Brown, 1910) to work by Richardson (1939), Kent (1940), Hollingworth and Taylor (1946) and Evans (1952), and the more recent studies by Downing and Williams (1969) and Booth (1981); however, the many decades of independent research has led to a plethora of confusing statigraphic names, restricted to certain localities. Ashton (1980) abandoned the traditional bipartite system and divided the formation into three informal units - the Upper, Middle and Lower Lincolnshire

Limestone. The revised system is summarised below and adhered to in the discussion of the geochemistry of the aquifer (chapters 5 and 6); however, as the original bipartite division is more appropriate to the construction of hydrological models, and the latter generally predate Ashton's study, it has been retained in the description of groundwater flow models (1.3.2).

1.2.1 Stratigraphy

Details of all the strata encountered in boreholes in the sampling area, are summarised in order of decreasing age, from Downing and Williams (1969), Booth (1981, 1983) and Ashton (1980). It should be noted that all the details refer to the outcrop and subcrop in southern Lincolnshire only. The Lincolnshire Limestone shows considerable facies variation along its strike, being a compressed sequence in the southern part, hence descriptions of the aquifer in central and north Lincolnshire are largely irrelevant to this thesis. The stratigraphy of the sequence is presented in table 1.1 and a generalised cross-section in figure 1.3.

Lias

At the base of some boreholes the Upper Lias is encountered, represented by grey clays and mudstones with thin limestone bands near the base. It is usually 42 - 52 m thick in southern Lincolnshire.

Northampton Sand

Together, these ironstones, sandy sideritic limestones and sideritic mudstones average 6m in thickness. Near outcrop they used to be an important source of iron ore.

Grantham Formation

Formerly termed the Lower Estuarine Series, this 6 m thick unit is characterised by fine, pale grey sands, greyish silts and silty clays, including seat-earths; subordinate calcareous

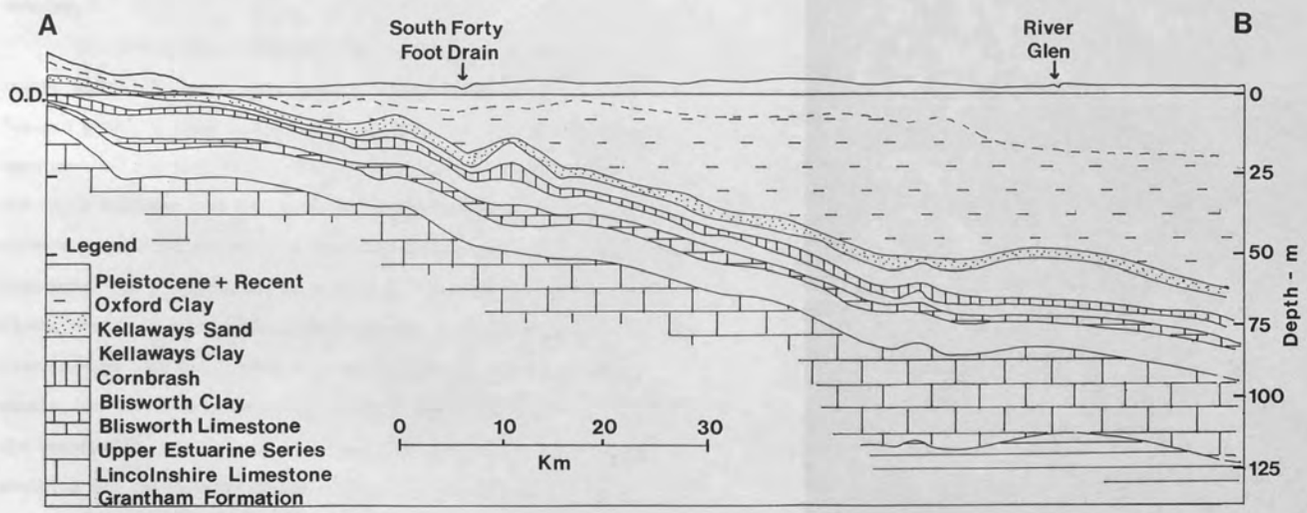
Table 1.1

STRATIGRAPHY			LITHOLOGY	THICKNESS (m)
Recent			alluvium, fenland gravels and sand, blown sand	variable
Pleistocene			boulder clay, glacial sand and gravel	variable
U.J.		Oxford Clay	clay with muddy limestones	c. 30
		Kellaways Beds	calcareous sandstone passing down into clay	0.6-6
M.J.	G.O.S.	Cornbrash	shelly limestone and ferruginous marl	0.3-3
		Blisworth Clay	clay and Shale	2-12
		Blisworth Limestone	limestone with thin marl and clay beds	2.5-8
		Upper Estuarine Series	sand, clay, shale and limestone	4.5-14
	I.O.S	LINCOLNSHIRE LIMESTONE	oolitic and argillaceous limestones, calcareous sandstones and cementstones	0-40
		Grantham Formation	sand, clay and shale	0-9
		Northampton Sand	ferruginous sand and sandstone	0-11
L.J.		Upper Lias	clay and shale with thin limestones	17-76

Strata associated with the Lincolnshire Limestone in southern Lincolnshire, modified after Downing and Williams, 1969. U.J., M.J. and L.J. = Upper, Middle and Lower Jurassic; G.O.S. = Great Oolite Series and I.O.S. = Inferior Oolite Series

Figure 1.3

General geological cross-section along the line of section (A-B) indicated in figure 1.2.



sandstones and carbonaceous clays also occur. Essentially the formation is an impermeable unit which confines the Lincolnshire Limestone aquifer from below.

Lincolnshire Limestone

For groundwater flow models, division into a lower, poorly-cemented, current-bedded and locally argillaceous unit, and an upper, massive, well-cemented shelly oolite with well-developed fractures is often sufficient. This is however, a gross generalisation, for the internal stratigraphy is considerably more complex.

The Lincolnshire Limestone was originally classified into two units, upper and lower, the boundary being at the level of the "*crossi* beds", a readily mappable limestone containing abundant specimens of the spinose brachiopod *Aconthothiris crossi*. However, the exact boundary was the cause of considerable debate, some authors placed the division between the Upper and Lower Lincolnshire Limestones above the *crossi* beds (Evans, 1952) and others below it (Kent, 1940). Ashton examined the internal relationships of the Lincolnshire Limestone along its entire strike, in considerable detail. Two major erosive horizons were identified that facilitated the county-wide division of the formation into three units, thus avoiding the controversy of the traditional Upper/Lower contact.

Rock core from Bicker borehole (discussed in chapters 5 and 6), has been logged in detail according to Ashton's (1980) revised stratigraphy by Emery (*pers. comm.*, 1985). The general lithologies and stratigraphy of Lincolnshire Limestone core encountered at Bicker are summarised in table 1.2. Details of the the revised stratigraphy appropriate to the aquifer in southern Lincolnshire are:

Table 1.2

STRATIGRAPHY		LITHOLOGY	THICKNESS (m)
Upper L.L.	Clipsham Member	granular and shaley limestone	1
	Sleaford Member	black crumbly oolite	2
		lime mudstone	1.6
		coarse oolite	0.8
		friable oolite	1.4
		hard fine-grained limestone	1
Middle L.L.	Lincoln Member	argillaceous limestone	0.25
		"*crossi* beds" clayey limestone	0.6
		oolite in clay matrix	2.4
Lower L.L.	Greetwell Member	fine-grained limestone	3.5
		pisolite	3.4
		oolite in clay matrix	3.3
		cemented oolite	1.3
		clayey limestone	0.6
		hard limestone	0.4

Summary of general lithologies encountered in Lincolnshire Limestone (L.L.) core from Bicker borehole. Approximate thicknesses only given. Source of data: D. Emery *pers. comm.* (1985).

(i) Lower Lincolnshire Limestone

(a) Sproxton Member: At the base, a 1.6 m thick unit varies from a massive silty or sandy limestone, to a blue-grey silty, dolomitic biomicrite. It is overlain by a stiff, black, well-laminated clay of approximately 0.3 m thickness.

(b) Greetwell Member: Sedimentary patterns are rhythmic, with peloidal, oolitic calcarenites overlain by a thinner unit of fine-grained, well-sorted pelsparites.

(ii) Middle Lincolnshire Limestone

Only the Lincoln Member is represented in southern Lincolnshire and it is divided into three units - Ropsley, Scottlethorpe and Castle Bytham Beds - all with mildly erosive contacts and totalling 3 m in thickness. The Ropsley Beds (1 m), comprise calcilutites with clay-marl partings; the Scottlesthorpe Beds range from rubbly-weathering, fossiliferous calcilutites to oolitic calcarenites and include all or part of the *crossi* beds; the Castle Bytham Beds consist of oolitic and sometimes peloidal calcarenites, grading into calcilutites.

(iii) Upper Lincolnshire Limestone

(a) Sleaford Member: The contact between the upper and middle divisions of the Lincolnshire Limestone is generally mildly erosive, however, in places the Sleaford Member downcuts deeply into the Lincoln member. The Sleaford Member comprises oncolitic calcirudites and cross-bedded skeletal and oolitic calcarenites, within which four facies can be identified: cross-bedded oolites, fining-up rhythms, coarsening-up rhythms and biohermal micrites.

(b) Clipsham Member: Cross-bedded oolitic calcarenites predominate, with impersistent subsidiary skeletal calcarenites to calirudites. Fossil assemblages in this 5 m thick unit show current-induced size-sorting.

Upper Estuarine Series

This freshwater sequence at the base of the Great Oolite Series unconformably overlies and confines the Lincolnshire Limestone and is 4-14 m in thickness. It is primarily composed of dark grey-green clays but there is a thin impersistent nodular limestone near the base. In places the Upper Estuarine Series and Lincolnshire Limestone are in hydraulic continuity.

Blisworth Limestone

Formerly termed the Great Oolite Limestone, this 3-8 m thick unit comprises blue-hearted shelly micrites with subordinate oolitic and marly beds. The Blisworth Limestone is a minor aquifer recharged via occasional swallow-holes at outcrop. The Upper Estuarine Series which separates the Blisworth and Lincolnshire Limestones is only of limited thickness, hence it is possible that groundwater movement can take place between the two aquifers.

Blisworth Clay

This formation averages 8 m in thickness and consists of distinctly coloured clays (purple, red and green) with shelly bands and ironstone nodules.

Cornbrash

The Cornbrash Limestone at the top of the Middle Jurassic, comprises a thin (3 m), persistent, indurated, bioclastic limestone, blue-hearted and massive when fresh, but weathering red-brown and rubbly. Although the strata are permeable, little groundwater storage is available because of their limited thickness. A spring-line is developed at the junction with the underlying Blisworth Clay and outliers form the "high ground" (over 10 m A.O.D), along the eastern limit of the sampling area.

Kellaways Beds

The Kellaways Clay consists of grey, poorly fossiliferous

mudstones, which are overlain by the greenish-grey, shelly, bioturbated, clayey silts of the Kellaways Sands.

Oxford Clay

This formation represents the youngest solid strata encountered in the boreholes in the field area, 'outcropping' over almost the entire area, though buried under a considerable thickness of recent deposits. The Lower Oxford Clay comprises rhythmically bedded, dark, fossiliferous and bituminous shales and pale, blocky mudstones with thin, pyritic shell beds. The Middle Oxford Clay consists of non-bituminous, less fossiliferous, calcareous mudstones.

Pleistocene

Approximately 15 m of boulder clay and outwash sand and gravels mask the solid geology of much of the Fenland area. In places, boulder clay also overlies the Lincolnshire Limestone at outcrop (figure 1.2); being impermeable, it inhibits the direct infiltration of precipitation, thus reducing the potential recharge of the aquifer (section 1.3.1).

1.2.2 Depositional Environments

During the Lias, argillaceous deposition in a transgressive sea was dominant. Bituminous marls in the Upper Lias are indicative of oxygen-deficient sea-bottom conditions. The base of the Middle Jurassic marks an onset of shallower conditions, as the Northampton Sand was deposited in a shallow, current-agitated shelf sea and the overlying Grantham Formation indicates brackish to freshwater marshland bordering on the London Platform (Wyatt, 1983).

The transgressive Lincolnshire Limestone succession is thought to represent the landward migration of an off-shore barrier complex across lagoonal and tidal flat deposits. The Lower Lincolnshire Limestone represents these latter environments, the

Middle unit comprises diverse agitated deposits, while barrier-bar, tidal inlet and tidal delta subfacies can be recognised in the Upper Lincolnshire Limestone (Ashton, 1980).

A period of erosion was followed by a return to freshwater and coastal marshland, during which time the Upper Estuarine Series was laid down. The fauna of brackish and marine bivalves represent periodic marine incursions. The Blisworth Limestone contains an abundant marine fauna but, as it grades up into the Blisworth Clay with oysters at the base and brackish bivalves in the upper part, a return to a restricted estuarine environment is indicated.

The Cornbrash was probably deposited in extensive, shallow, current-swept seas; later slight uplift of the land probably occurred. Following the deposition of the Kellaways Sands in shallow waters, there was a return to quiet argillaceous deposition. (Haines, 1969). The Oxford Clay and its fauna indicate anaerobic bottom-waters with episodes of current-activity and oxygenation; most of the Upper Jurassic sequence represents sedimentation in an open sea subject to little or no wave disturbance (Wyatt, 1983).

1.2.3 Diagenesis

Diagenesis of the Lincolnshire Limestone began even before deposition of the overlying Upper Estuarine Series commenced. Emery (1986) has studied the diagenetic sequence in detail and the following is a summary of his main conclusions.

In the marine realm, ooids (the chief inorganic carbonate precipitate) and skeletal material, were widely micritized through the activity of microborers; cementation was predominantly by high-magnesium calcite. During earliest burial of the more organic-rich sediments, the formation of pyrite was favoured by the combination of high sulphate-supply (sea-water), locally reducing micro-environments (associated with ooids and skeletal material),

sulphate-reducing bacteria and ferrous iron in solution due to the absence of refluxing oxygenated waters.

Sub-aerial exposure of the formation prior to the deposition of the Upper Estuarine Series allowed an initial influx of oxidising meteoric waters, causing widespread aragonite dissolution and stabilisation of high-magnesium to low-magnesium calcite. The latter was also a primary precipitate as echinoderm overgrowths. The freshwater lens was only a temporary phenomenon, hence the limited volume of this cement phase. Diagenesis in the meteroric realm was ultimately ended by a sea-level rise and alteration of the fluid-flow pattern in the sedimentary basin. The major clastic member of the formation - Kirton Shale (Middle Lincolnshire Limestone) restricted vertical fluid flow, thus oxidising waters circulated above it, while below it fluid flow became sluggish, and reducing at times, facilitating the precipitation of ferroan calcite. Where the Kirton Shale was absent, oxidising waters circulated to lower stratigraphic levels. A dissolution event predating the last phase of cement precipitation is tentatively explained by the influx of freshwater, unsaturated with respect to calcium carbonate, under temporary head-driven flow, during the deposition of the Upper Estuarine Series.

Diagenetic changes during burial include:

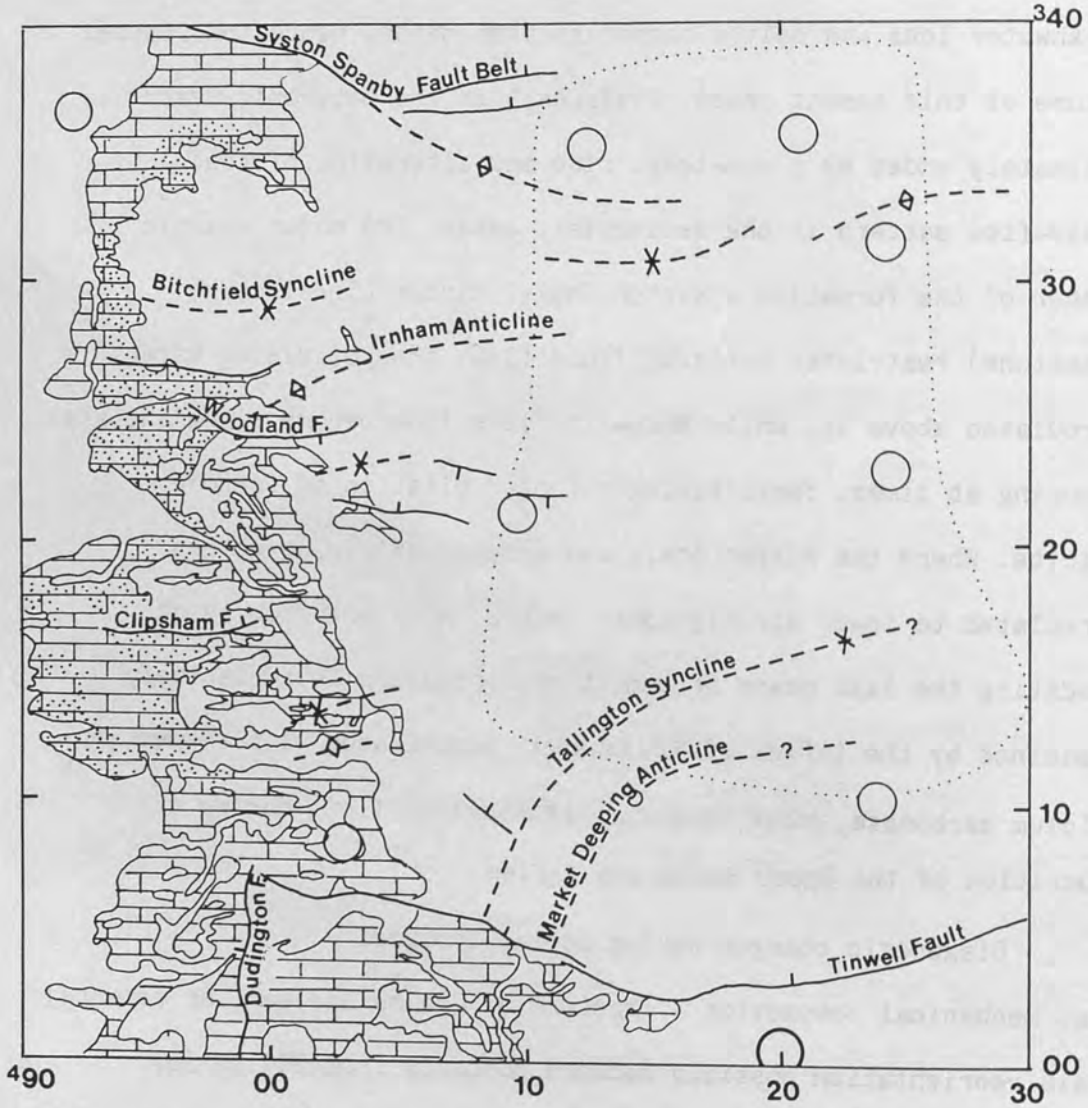
(a) mechanical compaction - fracture of grains and earlier cements; grain reorientation possibly reduced porosity from 50% to 35%.

(b) chemical compaction - pressure solution phenomena; soluble material (e.g. carbonate) dissolves at stressed grain-grain contacts and may be reprecipitated at some distance, insoluble material (clay minerals, organic matter, iron oxide etc.) is concentrated at solution seams/stylolites.

(c) cementation: non-ferroan burial calcite (5% of the total rock

Figure 1.4

Map of the outcrop (shaded) and major structural features of the Lincolnshire Limestone in southern Lincolnshire. The sampling area is enclosed in the dotted line, the stippling indicates the area of boulder clay cover and the towns (open circles) are as in figure 1.2. The downthrow of faults (solid lines) are marked with a tick, axes of folds are denoted by dashed lines and outward- and inward-pointing triangles represent anticlines and synclines respectively.



by volume); ferroan calcite (25% of the rock) and ferroan dolomite, requiring reducing conditions for the incorporation of ferrous iron in the carbonate lattice. Influx of remobilised carbonate from the Carboniferous Limestone, along faults between the two formations in the North Sea, is envisaged as a source of additional strontium, as required by the strontium isotopic composition of the Lincolnshire Limestone; alternatively, detrital clays, micas and potassium feldspar, either in argillaceous bands within the limestone, or in the confining formations, may have supplied the radiogenic strontium (Emery *et al.*, 1987). Dolomitization of the basal two members of the limestone occurred during progressive burial, the raised temperatures and reducing conditions facilitating the incorporation of magnesium and iron into the carbonate lattice. The problem of intervening calcite precipitation was not completely resolved.

1.2.4 Structure

In general, the structure of the Lincolnshire Limestone is simple, with a north-south strike and an easterly dip of one degree. The regional dip is less than in central and northern Lincolnshire, thus the flatter, wider outcrop has been dissected by rivers to a far greater degree, producing numerous inliers and outliers of the formation. The lower dip and more pronounced fissure pattern, enhanced by solution effects, has produced the rapid lateral flow paths of the unconfined zone in southern Lincolnshire (Downing and Williams, 1969).

The main structural features of the Lincolnshire Limestone are summarised in figure 1.5. Most of the folding and faulting follows a NW-SE to W-E trend, and includes the Burton Coggles and Tinwell faults, where the sequence is downthrown to the north by 23 and 55 m respectively. The N-S trending Dudington Fault has displaced the Lincolnshire Limestone by 30 m to the west (Downing

and Williams, 1969).

Some of the structural features further north are the result of synsedimentary phenomena; however, most of the folding and minor normal faulting in southern Lincolnshire, may be due to post-depositional tectonism, for example, during exposure of the formation prior to the deposition of the Upper Estuarine Series, during burial beneath the East Midlands Mesozoic sequence and at the end of the Cretaceous (Emery, 1986).

1.3 HYDROGEOLOGY

Prior to the development of the Lincolnshire Limestone aquifer as a groundwater resource on a large-scale, regional flow was down-gradient to the east from an area of recharge at outcrop. Discharge was predominantly via springs in the Glen catchment and artesian springs in the Fens. For decades each household had a small-diameter borehole tapping this artesian source, which supplied sufficient potable water for both domestic and agricultural use. However, the installation of larger-diameter, pumped boreholes for public water supply, close to the area of natural artesian discharge, resulted in a drying-up of springs in the lower reaches of the Glen catchment and a reduction in the area in which artesian conditions prevailed (Rushton *et al.*, 1982). Lowering of the water table in the unconfined zone also caused the direct infiltration of stream water and therefore a deterioration in water quality, while the lowering of piezometric levels around the principal abstraction sites, effected local reversal of the hydraulic gradient, i.e., the updip migration of saline water (Burgess and Smith, 1979). The local water authority was therefore forced to cease its practise of over-abstraction, and to initiate detailed research into the physical properties of the aquifer and possible groundwater flow mechanisms. The history of the development of hydrogeological models for the

Lincolnshire Limestone is reviewed in 1.3.2.

1.3.1 Recharge, discharge and fissure flow in the limestone

In a homogenous aquifer, regional groundwater movement is down the hydraulic gradient from an area of recharge to discharge. Rates of movement are controlled by the physical properties such as storage coefficient, porosity, hydraulic conductivity and transmissivity etc (appendix 1).

Recharge occurs via three principal routes:

(i) Direct infiltration by precipitation. The recharge area is covered to a large extent by Jurassic clays and boulder clay (figure 1.2) their relative permeability has a significant effect on infiltration characteristics (Rushton, 1975). Greater effective infiltration is possible in winter months when potential evaporation is at a minimum (Downing and Williams, 1969). Infiltration is calculated as:

Infiltration = Rainfall - Actual Evaporation - Surface Runoff

(ii) Swallow-holes. Surface runoff derived mainly from boulder clay overlying the outcrop, enters the limestone via the many swallow-holes, providing a source important in the "rapid recharge" concept of Fox and Rushton (1976), discussed later.

(iii) Influent seepage from streams. When a river with a permeable bed crosses an aquifer, water will infiltrate from the river and recharge the aquifer, if the water-table is lower than the river. At certain times of the year, the reverse conditions may occur, enabling groundwater to contribute to baseflow.

Discharge from the aquifer can occur in three ways:

(i) Streams; estimated at a loss of 22.5 Ml/day (Rushton, 1975).

(ii) Boreholes; it is estimated that about 70% of a typical year's recharge is abstracted (Rushton and Rathod, 1979), and most of this from the six water-supply pumping stations at Jockey, Bourne,

Wilsthorpe, Tallington, Etton and Pilsgate (Rushton, *op cit.*).

(iii) Flow to the east; Rushton's 12-year water balance suggests 1.8 Ml/day (2% of average infiltration) flows to the eastern part of the aquifer. However, this figure could arise simply from uncertainty from the water-balance calculation.

Oolitic rocks are generally porous; intergranular flow is normally significant. However, the Lincolnshire Limestone aquifer is characterised by secondary permeability with groundwater flow occurring predominantly via an extensively developed network of fissures and micro-fissures. The physical properties of 95 Lincolnshire Limestone samples from four cored boreholes - Cuckoo Bridge, Gosberton, Crowland Bridge and Tallington - were studied by Bird (1974). The wide range of mean porosities (13.6-19.0%) indicate the variable nature of the lithologies encountered. Permeabilities were low (0.04-0.71 millidarcies), giving hydraulic conductivities of the order of 10^{-5} to 10^{-4} m/day and very low intergranular transmissivities of approximately 10^{3} m/day. Pumping test analyses, however, gave high transmissivities of 10^{3} to 10^{4} m^2/day. The enormous difference between the two sets of results demonstrates the development of fissure-flow on an unusually large scale and the "almost total insignificance of intergranular permeability in groundwater flow."

The extensive fissure network, comprising vertical joints and bedding plane fractures, developed during tectonic and other structural movements, has been enlarged by weathering and dissolution. The fissure pattern was extensively developed during glacial periods by frost action, when the entire thickness of the Lincolnshire Limestone at outcrop must have been affected by permafrost (Downing and Williams, 1969). Solution of the limestone by groundwater itself, has also been significant in the development

of the fissures on all scales, particularly in the upper part of the limestone.

1.3.2 Groundwater flow models

Groundwater flow through aquifers can be simulated with resistance-capacitance analogue computers, in which electrical quantities are used to represent physical quantities: for example, capacitance for storage coefficient, voltage for piezometric head, current for quantity of flow. Such a system was developed at Birmingham University and applied to the study of flow problems in the Lincolnshire Limestone. Initial modelling extending over a one hundred year period, demonstrated that if abstraction from the aquifer was increased, dewatering would occur in the unconfined section of the aquifer; the drawdown of water levels in the confined region, would reverse the hydraulic gradient at depth, possibly causing an influx of saline water from the east (Rushton and Wedderburn, 1971).

The initial model was unable to predict the increase in piezometric heads noted in the artesian boreholes up to a month after heavy rainfall. To allow for this occurrence, additional transfer via fissures between the unconfined and confined section had to be incorporated in the model (Rushton, 1975). A time-dependent, mass-transfer routine, termed "rapid recharge" was developed. During periods of heavy rainfall, a proportion of the water intercepted by swallow-holes was transferred, via fissures, to the confined region, while some was stored in the unconfined section, and the rest discharged via streams. Water was not necessarily transferred immediately, it was thought that the inflow caused an increase in hydrostatic pressure resulting in a delayed transfer to the confined region (Fox and Rushton, 1976).

Addititional evidence for rapid flow has been obtained from

tracer studies. Booker (1977) demonstrated that rapid recharge of the water does occur and is discharged either via streams after a few days, or flows to the confined zone over a period of up to several months. Subterranean flow rates of 3-7 km/day have been recorded, between areas of recharge and spring discharge. From Fox and Rushton's (1976) rapid recharge model and Booker's (1977) tracer results, it has been concluded that the response of the aquifer is influenced by the magnitude of the recharge, rather than by the transmissivity or storage coefficient, but the overall groundwater gradient is controlled by the relatively low transmissivity of the bulk of the aquifer (Rushton *et al.*, 1982).

The drought of 1975/1976 followed by a winter of heavy rainfall, were extreme conditions that highlighted further inadequacies in the standard model (Rushton and Redshaw, 1979). Other features which had to be incorporated included a possible upper limit on the quantity of recharge accepted by the aquifer, the nature of the springs near outcrop and the variation of transmissivity and storage coefficient with saturated depth (Rushton *et al.*, 1982).

A two-layer model was proposed for the first time by Smith (1979). In this model the Lower Lincolnshire Limestone, a poorly-cemented, current-bedded and often argillaceous unit, is termed the primary zone and is characterised by a higher storage coefficient and lower transmissivity than the upper unit. The latter, termed the secondary zone, is a massive, well-cemented shelly oolite with more pronounced fractures. Rushton and Rathod (1979) refined this extension to the model, by incorporating the secondary system only when the primary zone is already saturated. The primary (lower) zone, with normal transmissivity, accepts recharge first and any remaining groundwater enters the secondary

zone, in which the transmissivity rapidly increases.

Downing *et al.*, (1977) related studies of groundwater age to flow mechanisms within the aquifer. They concluded that, while fissure-flow was the dominant method of fluid transfer to and in the confined region, 50% of water abstracted was "old interstitial water". They suggested that water in the limestone moved by slow displacement of water particles, a process analogous to "piston movement". Flow velocities through the matrix under natural conditions were estimated at 0.5 - 1.0 m/year near outcrop and 0.5 m/year in the eastern part of the confined zone. The interstitial fluid moves by pressure differentials and diffusion but once it enters a fissure can then be transported more quickly by fissure-flow.

1.4 HYDROCHEMISTRY

1.4.1 Chemistry

The hydrochemical variations which occur downdip, between calcium bicarbonate waters at outcrop and saline, supposedly connate waters, in the east, have been studied and documented in considerable detail, since Lamont (1958) identified a zone of soft water suitable for exploitation for public supply. Studies by Downing and Williams (1969), Edmunds (1973, 1982), Lawrence *et al.* (1976) and Downing *et al.* (1977) are of considerable importance in this field. Their findings are briefly summarised here and are discussed more fully in chapter 6.

Downing and Williams (1969), delineated five zones within the aquifer based on carbonate and non-carbonate hardness and dominant ions. Edmunds (1973) refined this description by examining the relationship of minor and trace element behaviour with that of major elements and processes such as ion exchange, oxidation- reduction and mixing with saline water. A "redox-barrier" was identified,

where the appearance of sulphide species due to bacterial sulphate-reduction, coincided with a drop in Eh and the disappearance of dissolved oxygen below the 0.2 mg l^{-1} detection limit. Resampling in 1979 produced very similar hydrochemical profiles, although the redox boundary was less distinct and the first appearance of sulphide species had shifted several kilometres to the east. An increase in sulphate and calcium levels was attributed to agrichemical contamination further downdip; however no concomitant nitrate concentration further to the east was recorded. It was concluded that the aquifer had a significant capacity for *in situ* nitrate reduction (Edmunds and Walton, 1983).

Lawrence *et al.* (1976) described mixing between bicarbonate-dominated fissure-waters derived at outcrop and old, sodium chloride-dominated pore-waters. The characteristics of their three zones are summarised here from Downing and Williams (1969), Edmunds (1973, 1982) and Lawrence *et al.* (1976).

The first zone extends from outcrop to 10-20 km downdip into the confined section. Dissolution of the limestone matrix by the aggressive recharge waters, causes an initial rapid increase in bicarbonate concentration. Across the zone the water becomes saturated or slightly oversaturated with respect to calcium carbonate and the bicarbonate concentration levels off. Sulphate-reducing bacteria, the presence of which is consistent with Eh-pH conditions, bring about a decrease in sulphate concentration and the production of hydrogen sulphide which can be detected at some well-heads. The increase in bicarbonate ions, brought about by this process is balanced by calcium carbonate precipitation, indicated by a decrease in TDS and calcium concentration.

In the interface zone, several changes occur over a very short distance: TDS, pH and chloride, bicarbonate and sodium

concentrations begin to increase; Eh begins to decrease; the decrease in sulphate concentration ceases and calcium concentrations decrease more rapidly. Ion exchange and mixing are thought to be the processes controlling these changes. Clay minerals within the Lincolnshire Limestone exchange sodium for calcium or magnesium and the increase in bicarbonate and chloride is attributed to mixing between old interstitial and younger recharge waters. A narrow (1.5 km wide) zone within the interface zone, represents the mixing and ion exchange front, while to the west the ion exchange capacity of the aquifer is considered to be virtually exhausted. The short distance of 15 km between the front and outcrop is a function of the low flow velocity downgradient, and its east-west fluctuation of up to 1 km is attributed to the seasonal balance between pumping and recharge.

The saline zone is restricted to the east of the confined section of the aquifer, where sodium and chloride are the dominant ions. The western limit is taken to be the 250 mg l^{-1} isochlor. Little is known of the water at depth, but it is assumed to approach seawater salinity fron evidence from boreholes in other parts of the aquifer (Andrews and Kay, 1982). It is also assumed to be of connate origin, that is, original marine water trapped in the carbonate sediments during deposition. A contribution from interstitial water from both underlying and overlying strata is possible. Seawater percolating down through the seabed during the Great Oolite marine transgression may have entered the limestone, and during compaction, formation water from the Lias clay may have been transported upwards into the aquifer.

1.4.2 Isotope Studies

The only data supporting the connate origin of the saline water were published by Andrews and Lee (1980). They identified a

simple correlation between ^{4}He and chlorinity and, by extrapolating chloride from a Spalding groundwater sample to seawater chlorinity, produced a groundwater age of 170 million years, i.e. in the middle of the Jurassic period. The results however, represent a considerable extrapolation of the data, possibly more than can be justified.

Other studies have demonstrated the influence of considerably younger water in the mixing process and flow mechanisms further updip. Downing *et al.* (1977) concluded from radiocarbon data, that the mean age of groundwater in the Lincolnshire Limestone increases downdip, until a maximum age of greater than 25000 years is attained, within 15 km of outcrop. Water east of the 100 mg l^{-1} isochlor generally has a mean age of greater than 9000 years and includes a significant component derived from Pleistocene precipitation. Values for δD and $\delta^{18}O$ values indicate that the temperature of recharge waters at the time was $8^{o}C$; as infiltration was prevented by frozen ground during winter at this time, it was suggested that recharge probably occurred during spring and autumn months. In the same study it was observed that the $\delta^{13}C$ values of the groundwaters became increasingly negative with distance from outcrop. The most likely interpretation was considered to be the continous dissolution and reprecipitation of calcium carbonate, confirming the results of an earlier study (Smith *et al.*, 1975).

Tritium, released into the atmosphere during thermonuclear explosions that began in 1953, has entered the confined section of the aquifer, and it is estimated that 50% of the water abstracted by public supply pumping stations such as Bourne, is derived from post-1953 rainfall. Andrews and Kay (1982), concluded from tritium results that the outcrop and western parts of the aquifer have been almost completely flushed with recent recharge. They estimate that,

at present rates of extraction, the entire storage in the aquifer would be completely flushed in 100-200 years. In the centre of the area, mixing of old interstitial water with the recent rapidly moving fissure-water is still occurring, as indicated by $^{234/238}U$ data. The rate of flushing is dependent on the rate of fissure and interstitial water exchange.

1.5 SUMMARY

Recent investigations into the hydrogeology and hydrochemistry of the Lincolnshire Limestone aquifer in southern Lincolnshire, have identified two components in the groundwater: recent recharge and old interstitial porewater. Recent recharge is transferred to the abstraction zone by an extensively developed fissure network, often in a matter of weeks. Tracer studies have proved flow velocities in the unconfined section of 3-7 km/day (Booker, 1977). Old interstitial water moves through the matrix at less than 1 m/year; when it diffuses into fissures, mixing between the two end-members can occur.

Although the piezometric gradient is downdip to the east, groundwater movement is not uniform in either direction or rate; the development of marls, for example, locally restricts groundwater movement (Downing and Williams, 1969). However, man's influence has considerably disrupted the natural flow regime in certain areas. Tritium concentration contours indicate that heavy abstraction in the Bourne-Wilsthorpe area has drawn older water from the east and the total westerly movement has been estimated at 5 km in the confined zone (Downing *et al.*, 1977). A seasonal balance between recharge and pumping has caused a general east-west fluctuation of 1 km in the potable/saline interface zone (Lawrence *et al.*, 1976), and one small source in a geologically isolated area has been closed due to the ingress of saline water from the east (Rushton, 1982).

CHAPTER TWO

2. COLLECTION OF GROUNDWATER AND ROCK CORE SAMPLES

2.1 INTRODUCTION

The criteria for the selection of sampling sites and the procedures employed in the collection of groundwaters are described, stressing the precautions required to avoid contamination. The treatment of cored rock from four boreholes prior to their dissolution, is outlined.

2.2 GROUNDWATERS

2.2.1 The selection of boreholes

Preliminary sampling of the area began in May 1984; seven boreholes in the saline zone were sampled, to gain experience in field techniques for groundwater sampling and on-site measurement. Over the following eighteen months, three separate trips to the sampling area were carried out at different times of the year, gradually expanding the area covered with every visit.

Suitable boreholes were selected with the help of staff from Anglian Water, who regularly test private supplies and maintain a network of observation wells. Most of the latter were purpose-drilled beside roads and were therefore the most accessible. Private supplies in constant use were also of high priority, as these boreholes are regularly flushed, ensuring the availability of representative groundwater within a short time. Occasionally-used domestic supplies were also sampled. The willingness of the owners determined whether sites were resampled, and in most cases they were very helpful. Some westerly boreholes towards the unconfined section of the aquifer were sub-artesian during the winter months, and could not be sampled on the final trip (December 1985).

The criteria for borehole selection were therefore primarily regular usage, ease of access and appropriate density of sampling

points. On the final trip a total of 49 sites were sampled (figure 5.1). All appropriate samples were taken for analysis on this sampling trip, these were for:

1. Major cation and trace element determination by inductively coupled plasma-optical emission spectrometry ICP-OES
2. Anion determination by automated colorimetry and ion-selective electrode (ISE)
3. Dissolved sulphide determination by ICP-OES and ISE
4. Rare earth element determination by ICP-OES
5. Strontium isotope measurement for D. Emery's project (see 2.1)

The analyses of these samples provide a comprehensive data-base on the hydrochemistry of the Lincolnshire Limestone, over a two-week period in December 1985. Data from samples collected on previous trips, together with earlier BGS data, provide information on longer term trends.

2.2.2 Collection of groundwater samples

2.2.2.1. Background

Between sample collection and analysis, the water is susceptible to alteration due to contamination from sampling and filtering equipment and from storage containers; modification of the chemical form of certain constituents, and by loss of ions by adsorption (Miles and Cook, 1981). Such alteration can be significant, particularly for trace elements. Sources of error reducing the reliability of subsequent analyses occur during sampling, filtering, preservation and storage.

To obtain a sample of water that is representative of that in the aquifer, it is essential to completely flush out water stored in the borehole. In steel-cased bores, acid reaction of the groundwater with the casing has been found to raise the pH, reduce the Eh, release metal ions into solution and increase the TDS concentration

(Marsh and Lloyd, 1980). However, even after complete flushing, water samples may still be contaminated by the casing, for example by abrasion of corrosion products from the lining by flowing water. Filtration of the water was therefore recommended to remove any suspended contamination products.

Groundwater samples are usually filtered through a membrane filter of 0.45 µm pore size on site. This choice of pore size is quite arbitrary however, and the division of water into suspended and dissolved fractions at 0.45 µm purely convention (Cook and Miles, 1980). Although such filtration is a standard procedure in groundwater sampling, whether or not it is necessary is a moot point. Unlike surface waters, the amount of suspended matter in groundwaters is extremely low and very little material is retained by the filter. Indeed on many occasions the difference between analyses of filtered and unfiltered duplicated samples carried out at BGS, has been seen to be negligible (D.L. Miles, *pers. comm.*). The procedure may even be disadvantageous, as contact of the water with filtration equipment can modify the trace element composition by contamination or adsorption (Marvin *et al.*, 1970).

Kennedy *et al.* (1974) demonstrated that a pore size of 0.1 µm should be used in preference to 0.45 µm, as some clay particles were not retained by the larger filter. During storage, the acid added to stabilise the water sample attacked the clays, yielding additional dissolved trace elements such as iron, titanium, aluminium and manganese. Moreover, the concentration of these elements was variable, as the degree of filter clogging determined the proportion of clays entering the filtrate. Use of the smaller filter increases filtration time however, and despite the debate the use of a 0.45 µm filter is still common practice.

Ideally, water samples should be analysed as soon as possible

after collection, as the loss of analytes can be brought about by the metabolic processes of micro-organisms and adsorption on container surfaces etc. Microbial activity may be suppressed by refrigeration at four degrees Celsius, or by the addition of mercuric chloride, chloroform, or an appropriate alkali or acid. The latter also prevent floccolation, precipitation and adsorption of certain metals (Anon, German Chemists Association, 1981). Immediate acidification to pH 1.5-2 with nitric acid was recommended by Robertson (1968) and Struempler (1973) and with hydrochloric acid by Subramanian *et al.* (1978). Any reagents added to the sample should be of appropriate purity in relation to the concentration of the elements to be determined.

The choice of container material for water sample storage is of critical importance if trace elements are to be determined. For most purposes, polyethylene or polypropylene is superior to glass, avoiding possible exchange of alkali metal ions, particularly boron, from the glass (Thompson and Walsh, 1983). Screw-caps should be of the same material as the container body and coloured plastics and cardboard inserts must be avoided (Cook and Miles, 1980). Contamination from sample containers is minimised by thorough cleaning before use, with high purity acid leaches followed by copious rinsing in distilled, deionised water. Moody and Lindstrom (1977) suggested that as nitric and hydrochloric acids appeared to leach different elements with different efficiencies, week-long leaches with both acids should be incorporated in the cleaning programme.

2.2.2.2 Field-work procedures employed

Before each period of field-work, all equipment was checked, fresh buffers and reagents prepared fresh as appropriate, and storage bottles thoroughly cleaned. The cleaning procedure included

leaches for up to one week in 50% v/v AnalaR HCl, 10% v/v AristaR HCl and finally distilled, deionised water until departure. Screw-cap polyethylene bottles of 250 ml, 500 ml and 5 l capacity and 30 ml Sterilin tubes, were used.

Groundwater was initially run to waste for 10 to 35 minutes, depending on the borehole's usage, to completely flush out the bore and pipe-work. Samples were filtered through a 0.45 µm pore size membrane filter. At many sites, artesian pressure was sufficient for a plastic Millipore in-line filter accessory to be used; however, low flow and/or the pipe-work arrangement precluded on-site filtration at several sites. These samples were filtered on return to the laboratory; their trace metal content was found to be higher than that of samples that were filtered in the field and are thus regarded as "contaminated" in later discussions of trace metal distributions in the Lincolnshire Limestone groundwaters (6.3.3.1).

All sample bottles were rinsed with filtered sample before filling to the top, acidifying with AristaR HCl to 1% v/v, tightly securing the cap and additionally sealing with Parafilm.

Dissolved oxygen and certain unstable parameters - Eh, pH, conductivity, alkalinity and temperature, were determined on-site using portable equipment. Dissolved oxygen was determined with an Orion Clark-type membrane electrode, screwed into a flow-through cell. It was calibrated for electronic zero and water-saturated air and the concentration of oxygen in the sample read off a pH/mV meter, down to 0.2 mg l^{-1}.

For Eh (redox potential), the potential developed at a platinum electrode was monitored in a flow-through cell. The absolute millivolt reading from the mV/pH meter was then corrected for the known reference electrode potential developed at the same temperature, for example +251 mV at 10°C. pH was determined

potentiometrically with a glass electrode and pH meter, calibrated against appropriate buffer solutions (Cook and Miles, 1980). Specific electrical conductance ($\mu S\ cm^{-1}$) of the sample at 25°C, was determined using a Phox electrode and meter with an automatic temperature-correction facility.

Carbonate species are the prime contributors to alkalinity in groundwaters and since carbonate equilibria are extremely unstable, determination of alkalinity in the field is preferable. Using a Hach digital titrator, 0.16N sulphuric acid was titrated against 100 ml sample containing a few drops of bromocresol green indicator, which changed from blue to a straw colour at an end-point of pH 4.5. Alkalinity was expressed as an equivalent concentration of HCO_3.

2.3 ROCK CORE

Three boreholes in the saline zone which had been lithologically logged in detail, were selected as sources of rock core (figure 5.1): Bicker and Donington boreholes in the north-east of the area (logged by D. Emery) and Moulton West Fen in the south-east (logged by BGS). Core from a former BGS borehole near Billingborough in the north-west, was also analysed to compare the geochemistry of normal grey and oxidised buff Linconshire Limestone samples.

A total of 24 samples representative of the Lincolnshire Limestone and overlying lithologies were taken from the three easterly boreholes. They were carefully wrapped and returned to the laboratory. The samples were rinsed and dried to remove any dust from rock-chippings in the core-boxes, then reduced to a fine powder using a steel jaw-crusher and Tema-mill. To prevent cross-contamination, the equipment was "hoovered", rinsed, dried with acetone and a small portion of the sample processed and discarded between each sample. The steel swing-mill was, in

particular, a potential source of contamination, however, in a comparison of duplicate samples using the steel and agate mill, the differences between the analyses was found to be less than the precision for the determinations (4.6).

Having taken such precautions to prevent inter-sample and equipment contamination, the powders were bagged until required for drying, weighing and dissolution as described in 3.3.2.

2.4 SUMMARY

During sample collection and preparation of both groundwaters and rocks, constant care was taken to prevent contamination, particularly in samples for trace element analysis. Potential sources of contamination include equipment for groundwater sampling, filtering and storage and rock crushing, which were all thoroughly cleaned before use. Reagents added for the preservation or dissolution of samples, were of appropriately high purity.

CHAPTER THREE

3. ANALYTICAL METHODS FOR THE ROUTINE ANALYSIS OF ROCKS AND GROUNDWATERS

3.1 INTRODUCTION

The release of the first commercial instruments for inductively coupled plasma-optical emission spectrometry (ICP-OES) was greeted with considerable enthusiasm. The technique appeared to offer the simultaneous determination of twenty to forty elements over a wide concentration range, with excellent detection limits, good precision and freedom from matrix and spectral interferences. Experience with ICP-OES demonstrated that such high expectations could not be realised; however, it is a powerful technique; facilitating relatively cheap, simultaneous multielement analysis; it has many applications in geochemistry.

The majority of the determinations in samples from the Lincolnshire Limestone aquifer, were performed by ICP-OES. Two instruments were employed: an ARL 34000C for groundwater analysis at BGS, Wallingford; and a Philips PV8490 used both at King's College and RHBNC geology departments. The principles of ICP-OES and a comparison of the two instruments are presented, sample preparation techniques outlined, and routine procedures employed in geochemical and water analysis described. Finally other analytical methods used for the analysis of Lincolnshire Limestone samples are listed.

Non-routine ICP-OES applications are described in chapter 4.

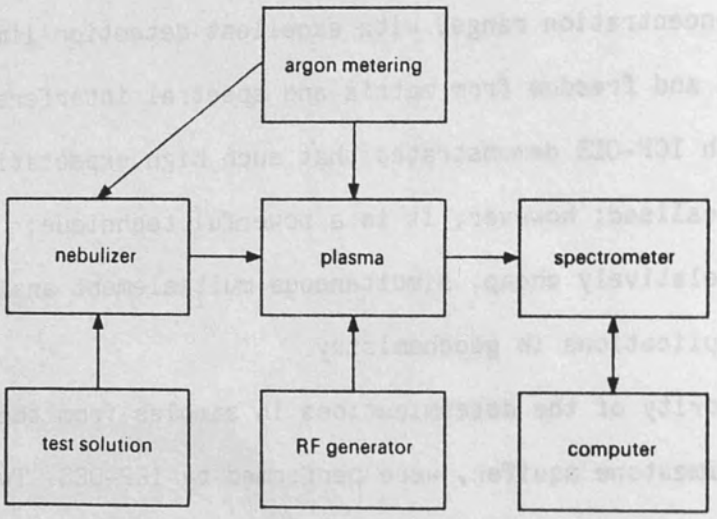
3.2 PRINCIPLES OF ANALYSIS BY ICP-OES

3.2.1 Introduction

The early development of the inductively coupled plasma (ICP) as an excitation source and its subsequent use with purpose-built spectrometers for geochemical analysis, has been well documented (Greenfield *et al.*, 1965, 1976; Wendt and Fassel, 1965; Boumans and

Figure 3.1

Schematic representation of an ICP-OES system with conventional pneumatic nebulisation (after Thompson and Walsh, 1983).



de Boer, 1975; Scott *et al.*, 1974; Thompson and Walsh, 1983; Fassel, 1986 etc.) The history of the technique is not presented here, however the principles of ICP-OES will be summarised and the essential differences between the Philips and ARL instruments outlined.

Solids and gases have been successfully analysed by ICP-OES (3.2.2), however this account will be mainly restricted to a discussion of solution analysis, exemplified by the analysis of groundwater samples and solutions of rock samples from the Lincolnshire Limestone aquifer.

There are four essential components in ICP-OES.

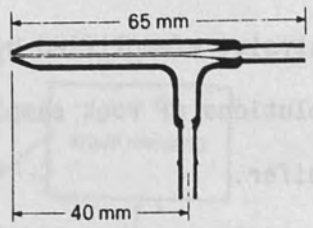
1. The **sample introduction system** converts the sample solution into a fine aerosol and comprises a nebuliser and spray chamber.
2. The **excitation source** is the ICP itself, a high temperature ionised gas (argon) in which molecules are dissociated and atomic and ionic excitation occurs. Energy is supplied by a radio-frequency (RF) generator.
3. An **emission spectrometer** measures the intensity of atom and ion lines in the visible and ultraviolet regions of the spectrum. Preselected spectral lines may be measured simultaneously or sequentially according to the design of the spectrometer.
4. A dedicated **computer** quantifies the intensity of each spectral line via stored calibration information, emission intensity usually being linearly related to analyte concentration over several orders of magnitude.

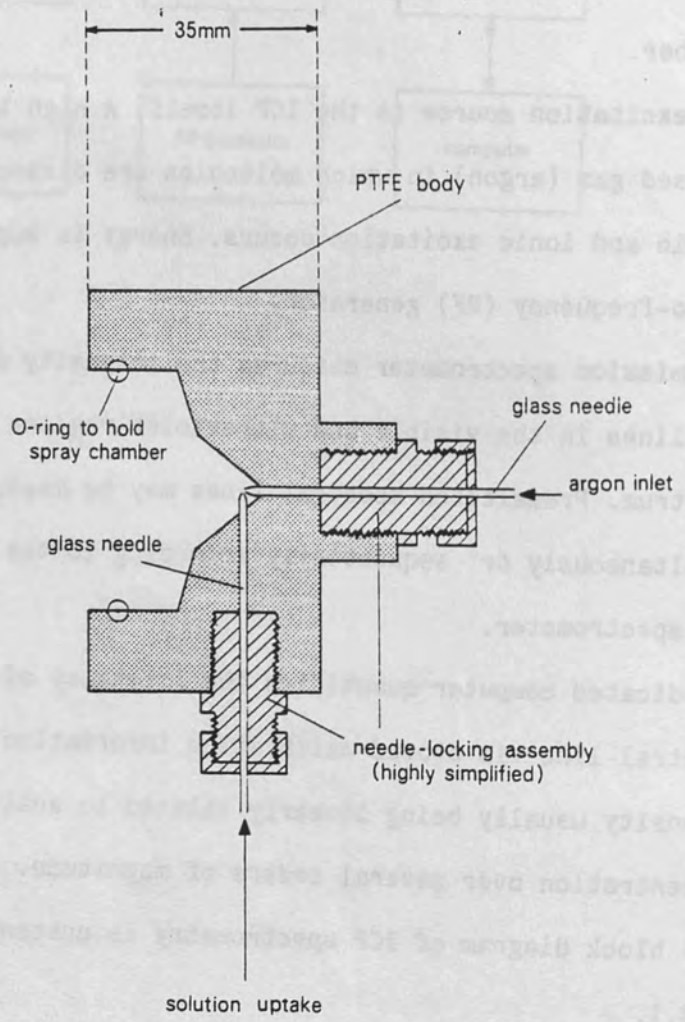
A block diagram of ICP spectrometry is presented in figure 3.1.

Figure 3.2

Nebulisers used for routine ICP-OES analysis

Groundwaters are aspirated into the ARL ICP by a Meinhard nebuliser (upper diagram). The lower diagram is a simplified drawing of a cross-flow nebuliser as used in conjunction with the Philips ICP system (after Thompson and Walsh, 1983).





3.2.2 Sample Introduction

Samples are most commonly presented to the ICP as a solution. While waters are already in an ideal form for presentation, a dissolution procedure is required prior to the analysis of geochemical or biological samples, introducing the possibility of contamination and increasing the time and cost of sample preparation. However, the advantages of presenting solutions rather than solids or slurries include the presentation of a homogeneous sample, minimisation of matrix effects and the availability of a number of separation and preconcentration techniques (Walsh and Howie, 1986).

Sample solutions are usually introduced via a pneumatic nebuliser and spray chamber. For efficient aerosol transport to the plasma with subsequent rapid desolvation, volatilisation and atomisation of the droplets, the nebuliser must generate an extremely fine aerosol, ideally less than 10 μm in diameter. In practise a highly polydisperse aerosol is generated, the droplet size extending to 100 μm or more. The larger droplets are shattered by impact in the spray chamber or are collected and drained to waste. In order to obtain efficient aerosol generation in the desirable small droplet range, it is necessary to maintain a high gas velocity in the nebuliser; however, the gas flow patterns of the plasma itself restrict argon flow rates that are feasible in the nebuliser/spray-chamber, typically to 0.8-1.2 l min^{-1}. By employing extremely fine orifices for both gas and liquid flow, relatively high velocities are generated in the nebuliser, overcoming the problem of the low argon flow rates.

The two most popular designs of pneumatic nebuliser are the Meinhard (concentric) and cross-flow models (figure 3.2). The former has a fine annulus for the gas flow, surrounding a central capillary

for the sample solution; in a cross-flow nebuliser the tip of the vertical sample delivery tube is crossed by a horizontal jet of argon. Relatively high gas flow through the annulus or horizontal tube reduces the pressure at the tip of the sample delivery tube, drawing liquid up the central capillary or narrow vertical tube of the concentric and cross-flow nebuliser respectively.

A six-roller peristaltic pump is used in conjunction with the Philips instrument, as cross-flow nebulisers are generally not self-priming. Pumping allows the operator to control the sample solution uptake rate, should for example, the viscosity of the solutions alter, although this is usually avoided by judicious sample and standard matrix-matching. The problem of viscosity variation should not occur in groundwater samples and the combination of a Meinhard nebuliser and pump can unnecessarily prolong stabilisation time (Thompson and Walsh, 1983); the Meinhard nebuliser in the ARL 34000C is therefore self-feeding. The aspiration rate is set by the interaction between the differential pressure drop from the nebuliser tip, to the solution head in the sample container, and the orifice diameter in the nebuliser (Browner *et al.*, 1982).

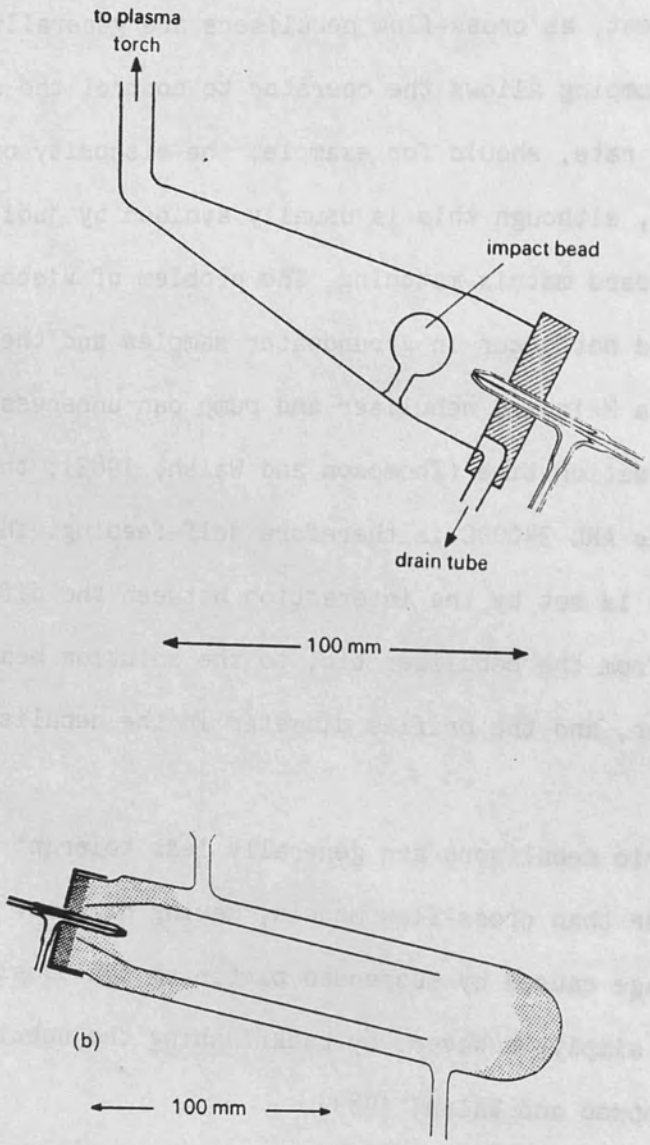
Concentric nebulisers are generally less tolerant of suspended matter than cross-flow models, having narrower sample tubes. A blockage caused by suspended particles can usually be removed fairly simply, however, by backflushing the nebuliser using a syringe (Thompson and Walsh, 1983).

"Salting-up" is not generally a problem during the aspiration of dilute groundwaters and is minimised by using humidified gas; the nebuliser argon for the ARL system is first saturated with water vapour by bubbling it through a reservoir before it enters the instrument. The problem is more serious, during the analysis of

Figure 3.3

Spray chambers routinely used in ICP-OES

The upper diagram shows a spray chamber with impact bead used in conjunction with a Meinhard nebuliser, as in the ARL system. The double-pass spray chamber employed in the Philips system has a large dead-volume, indicated by shading in the lower diagram (after Thompson and Walsh, 1983).



highly concentrated solutions, particularly those containing low-solubility salts such as sulphates. A study by Sharpe (reported in Thompson and Walsh, 1983) illustrated that droplets recirculating in eddy currents near the nebuliser tip may fall back onto the tip, evaporate and gradually block the annular gas orifice. Progressive obstruction of argon to the ICP leads to plasma instability and eventually extinction. Baginski and Meinhard (1984) demonstrated however, that salt deposits accumulate in the sample delivery tube in the torch, rather than in the nebuliser. By incorporating a "recessed capillary tip nozzle" in the nebuliser, the period of time prior to plasma extinction was notably increased. They noted that a crystalline collar formed around the recessed capillary and annulus of the nebuliser, only when it remained in the spray-chamber after plasma shut-down, without first aspirating 1M HCl solution. Cobbold (1986) noted that blockages in the sample delivery tube of the torch could be avoided by using a modified model, without a constriction close to the tip. When **nebuliser** blockage became apparent during the aspiration of certain high TDS solutions, an improvement was effected by selecting an alternative background matrix.

The two types of spray chamber used in the Philips and ARL instruments are shown in figure 3.3. The Philips system employs a Scott double-pass chamber in which the aerosol is forced down an inner tube and back up an outer concentric tube, before passing to the torch. By separating forward and reverse aerosol flows, turbulence within the chamber and condensation on the nebuliser is reduced, thereby improving plasma stability (Scott *et al.*, 1974). There is a substantial dead volume however, which is not sufficiently swept by the gas flow, necessitating a relatively long cleanout period to ensure the complete removal of the test solution before integration begins on the next sample (Ramsey *et al.*, 1983).

The Fassel-type, single-pass chamber used in conjunction with the ARL ICP is much smaller and has an impact bead 10 mm from the nebuliser tip to aid the shattering of aerosol droplets. In both spray-chamber models, the coarser droplets deposit on the glass walls, recombine at the base of the chamber and flow to waste through a drain tube. The drain passes through a permanently-filled water trap, which maintains sufficient overpressure in the chamber to force the argon and aerosol to the torch.

Browner *et al.* (1982) described a model of aerosol generation during its passage from nebuliser to plasma, identifying three aerosol populations. The primary aerosol emerges from the nebuliser tip into the spray chamber. Through impact with the chamber walls and impact devices, larger droplets are removed, small droplets follow the gas stream and intermediate droplets of sufficiently high velocity may shatter and generate smaller droplets. This secondary droplet distribution is further modified through the processes of impaction, turbulence, gravitational settling and evaporation etc. Droplets greater than 5-10 µm are thus collected and removed by the spray chamber, while the tertiary droplet distribution of the aerosol is transported to the plasma.

The design of nebulisers, spray-chambers and impact devices is of critical importance to the distribution of the tertiary aerosol, the production of memory effects, inter-sample cleanout time required, the fluctuation of the analytical signal caused by volatilisation interferences and to the percentage of sample reaching the plasma (e.g. Olsen and Strasheim, 1983; Ramsey *et al.*, 1983; Willis, 1986; O'Grady *et al.*, 1986).

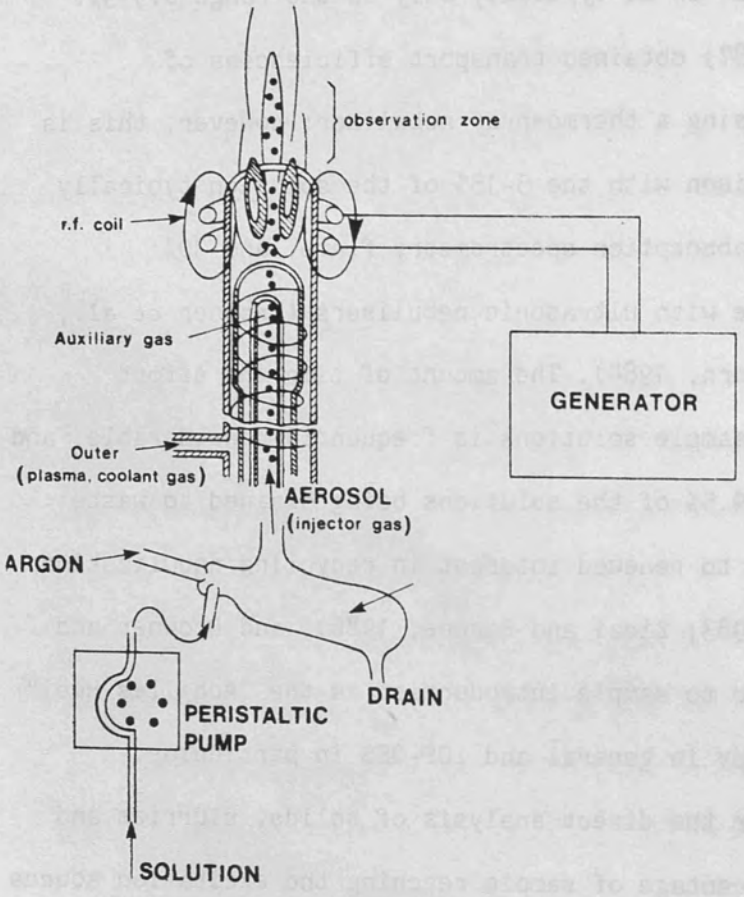
The proportion of the analyte reaching the plasma, that is, transport efficiency or nebulisation efficiency (En), is defined as the ratio of analyte entering the ICP to the amount of analyte

aspirated (IUPAC, 1976) and is commonly expressed as a percentage. Numerous studies (e.g. Scott *et al.*, 1974; Olson *et al.*, 1977; Ebdon and Cave, 1982; Smith and Browner, 1982; Maessen *et al.*, 1984; Schwartz and Meyer, 1986; Dale and Buchanan, 1986), have been carried out with different combinations of commercial and laboratory-built pneumatic nebulisers and spray-chambers, but all have demonstrated that En is typically only in the range 0.5-3%. Vermeiren *et al.* (1987) obtained transport efficiencies of approximately 3.5% using a thermospray nebuliser; however, this is still poor in comparison with the 5-15% of the solution typically reaching the atomic absorption spectrometry flame, and 30% efficiencies possible with ultrasonic nebulisers (Browner *et al.*, 1982; Browner and Boorn, 1984). The amount of time and effort required to prepare sample solutions is frequently considerable, and the prospect of 97-99.5% of the solutions being drained to waste immediately, has led to renewed interest in recycling nebulization systems (Hulmston, 1983; Zicai and Barnes, 1986), and Browner and Boorn (1984) to refer to sample introduction as the "Achilles Heel" of atomic spectroscopy in general and ICP-OES in particular.

Techniques for the direct analysis of solids, slurries and gases, where the percentage of sample reaching the excitation source is potentially much greater, and therefore the percentage of sample immediately lost to waste much smaller, have been the subject of considerable research. These include electrothermal vaporisation or volatilisation (Gunn *et al.*, 1978; Browner and Boorn, 1984; Hull and Horlick, 1984; Park and Hall, 1986; Long and Snook, 1983; Ogaram and Snook, 1984; Kitazume, 1983); laser ablation (Thompson *et al.*, 1981a); fluid inclusion decrepitate analysis (Alderton *et al.*, 1982); and slurry nebulization (Ebdon and Cave, 1982; Ebdon and Wilkinson, 1987).

Figure 3.4

Schematic representation of the sample introduction system and ICP source of the Philips ICP-OES system (after Walsh and Howie, 1986)



3.2.3 The excitation source

The argon inductively coupled plasma (ICP) is a partially ionised gas consisting mainly of argon atoms (Ar), argon ions (Ar^+) and electrons (e^-) (Blades and Horlick, 1982). It is formed at the open end of a quartz torch through which the argon and sample aerosol are introduced. The argon is constrained into three concentric streams (figure 3.4): the innermost tube transports the "carrier" or injector gas plus the sample aerosol from the spray-chamber to the plasma; the "coolant" gas flows along the outermost tube to prevent the plasma melting the torch and the "auxilliary" gas flows between them.

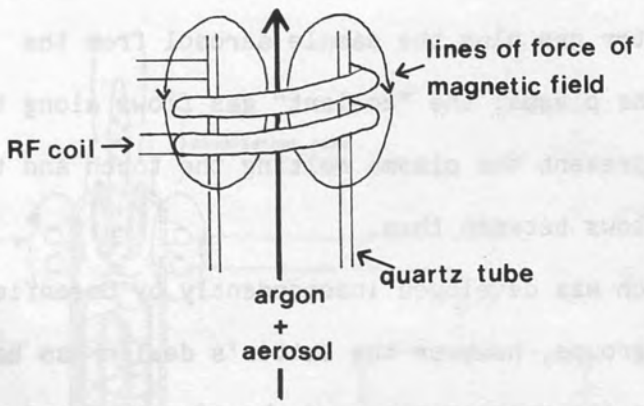
The ICP torch was developed independently by Greenfield's and Fassel's research groups, however the latter's design has been the most popular due to its smaller size and therefore reduced gas consumption. Typical argon flow rates in modern commercial ICP torches are 10-20 l min^{-1} for the coolant (outer) gas; 1 l min^{-1} for the carrier (inner) gas and 0-1 l min^{-1} for the auxilliary (intermediate) gas (Thompson and Walsh, 1983).

The top of the torch is surrounded by a two or three-turn induction coil carrying a high frequency current from an RF generator. A rapidly oscillating magnetic field is initiated whose lines of force are oriented axially in the torch and follow closed elliptical paths around the coil (figure 3.5). The argon is initially made conductive by the discharge of a tesla coil which introduces "seed" electrons into the magnetic field. As the argon passes up the torch, the RF field encounters resistance from the ionised gas and ohmic heating results. Inductive heating is then sufficient to maintain a stable plasma at 6000-10000 K.

The RF generator which provides the high frequency current is one of two basic types: "crystal-controlled", which use a

Figure 3.5

ICP formation (schematic). Argon passes through the lines of force of the magnetic field which follow closed elliptical paths around the RF coil.The plasma is ignited by a high voltage discharge from a Tesla coil and is sustained by induction heating from the RF coil, which operate at approximately 2 Kw.



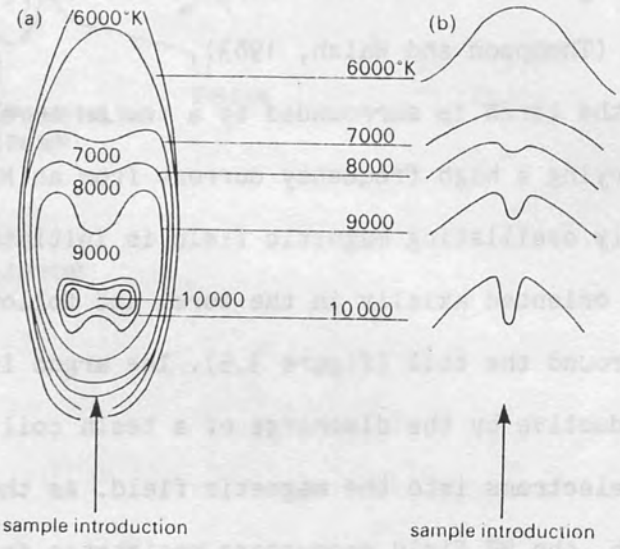


Figure 3.6

Temperature profile of a typical ICP in degrees Kelvin, with the cross-sectional view in diagram (b) (after Thompson and Walsh, 1983)

piezoelectrical crystal to maintain the constant frequency of the oscillating current, and "free-running" generators in which the frequency is allowed to change with alteration in the plasma impedance. The ARL generator runs at 27.12 mHz and is crystal controlled, the Philips operates at 50 mHz and is free-running.

The carrier gas and sample aerosol pass up the centre of the toroidal plasma, where the temperature is significantly cooler than that of the surrounding plasma. The characteristic temperature profile of an ICP is shown in figure 3.6. As the sample passes through this cooler axial tunnel, it is heated from the outside, volatilised and atomised. The relatively long residence time in the inert plasma and the high temperatures encountered ensure the virtually complete breakdown of sample molecules, efficient excitation and reduces the possibility of chemical interferences. Unlike other plasmas and flames, the sample is heated from the outside, thus reducing the possibility of self-reversal or self-absorption occurring, which reduce emitted radiation and result in non-linear calibrations.

A complex spectra of atom and ion lines from many elements is emitted from the bright tail flame above the plasma. The emission lines include traditionally difficult refractory elements (Walsh and Howie, 1986), for example chromium and titanium. This region is used for spectroscopic observation and measurement, usually 12-20 mm above the load coil. However, as spectral lines are generated at different heights in the tail-flame, a compromise viewing height above the coil has to be selected for routine analysis.

3.2.4 Measurement of emission intensities of spectral lines with the spectrometer

The intensities of the analyte spectral lines are monitored in both the Philips and ARL instruments by Paschen-Runge type

Table 3.1

COMPARISON OF PHILIPS AND ARL ICP-OES INSTRUMENTS

MODEL	Philips PV8490	ARL 34000C
NEBULISER	Cross-flow	Concentric glass
		(J E Meinhard TR-30-A3)
SPRAY CHAMBER	Scott-type, double pass	single-pass + impact bead
PUMP	6-roller peristaltic	none
POLYCHROMATOR	Philips PV8210	ARL 34000C Quantovac
	1.5 m, airpath	1 m, vacuum
Mounting	Paschen-Runge	Paschen-Runge
Grating	Holographic	Ruled: 1080 grooves/mm
SCANNING	SOPRA F400	ARL 35000
MONOCHROMATOR	1 m, vacuum	1 m, airpath
RF GENERATOR		
Frequency	50 mHz	27.12 mHz
Oscillator	free-running,Colpitts C	crystal-controlled
Power Output	0.7 - 2 kW	1.2 - 2.5 kW
Cooling	fan-driven air current	aircooled
	water cooled heat exchanger	
COMPUTER	Philips P851	PDP-11/03
readout	1 X 10 sec. integration	mean of 3 X 10 sec. ints.

spectrometers which have numerous fixed exit slits. Essentially, the light emitted from the plasma tail-flame is focused by the entrance optics (lens and primary slit) onto a diffraction grating; the diffracted light is focused onto photomultiplier tubes on the Rowland circle, arranged at positions corresponding to the specific wavelengths of the individual spectral lines of interest. The light energy is converted to electrical signals proportional to elemental emission intensities.

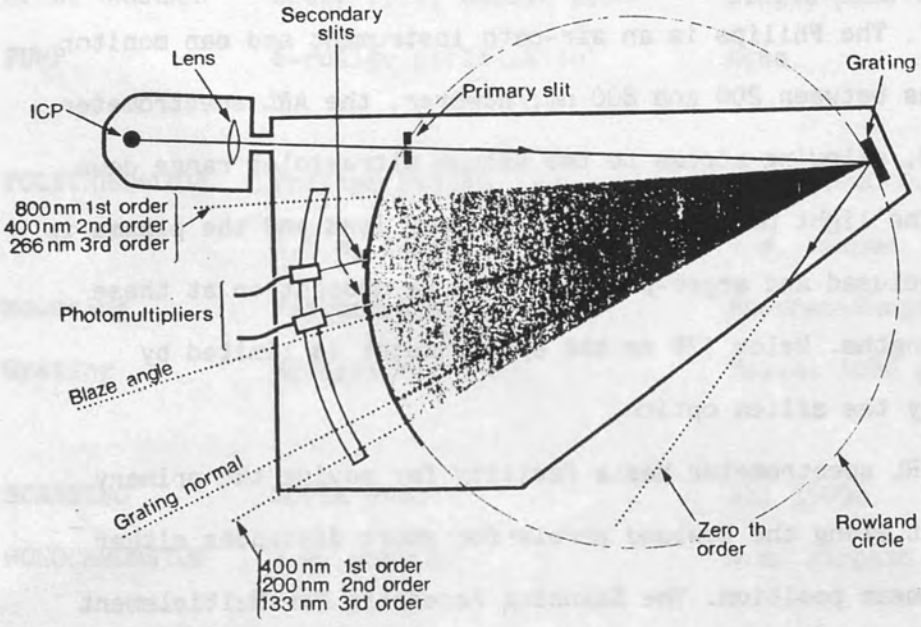
There are several essential differences between the Philips PV8210 and ARL 34000C Quantovac spectrometers, which are summarised in table 3.1. The Philips is an air-path instrument and can monitor analyte lines between 200 and 800 nm; however, the ARL spectrometer is evacuated, allowing access to the vacuum ultraviolet range down to 170 nm. The light path between the primary lens and the plasma is therefore enclosed and argon-purged to reduce absorption at these lower wavelengths. Below 170 nm the spectrometer is limited by absorption by the silica optics.

The ARL spectrometer has a facility for moving the primary entrance slit along the Rowland circle for short distances either side of its mean position. The Scanning Accessory for Multielement Instrumentation (SAMI), consists of a computer-controlled stepper motor-drive mechanism which moves the primary slit from side to side in precisely controlled increments, causing the spectrum to move across the secondary slits, thereby allowing the spectral environment around each analyte wavelength to be checked. This is particularly useful for revealing line to background relationships and for resolving ambiguities concerning analyte peaks, for example background shifts, spectral interferences and reagent impurities.

Light from the primary slit is diffracted to the exit slits by a concave grating, either of replica ruled or holographic design.

Figure 3.7

The optical system of a polychromator in the Paschen-Runge mounting with the diffraction grating blazed for a maximum reflection of 600 nm in the first order (after Thompson and Walsh, 1983).



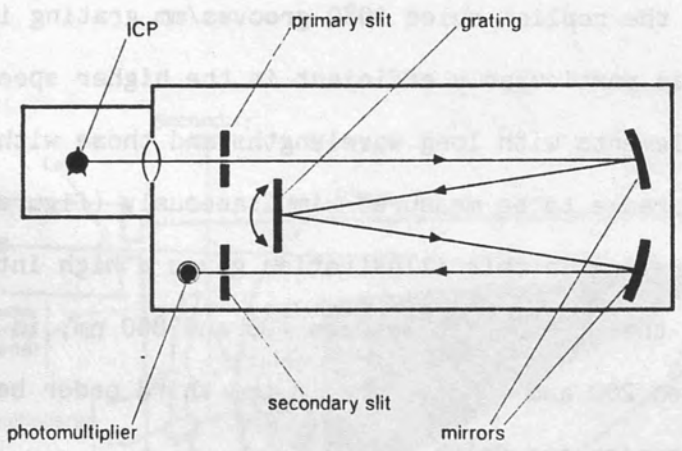
A holographic grating is produced by a photographic process from interference fringes formed by laser light and is incorporated in the Philips spectrometer. It is considered superior to ruled gratings on several counts: holographic gratings tend to be larger, providing better resolution; a cleaner spectrum can be obtained as less stray light is generated, and they are free from the imperfections which can cause "ghosting" in the spectra; they are also usually cheaper. However, the higher order spectra are of low intensity, whereas the replica ruled 1080 grooves/mm grating in the ARL spectrometer, is particularly efficient in the higher spectral orders, enabling elements with long wavelengths and those with lines in the ultraviolet range to be measured simultaneously (figure 3.7). The spectrometer grating in this illustration gives a high intensity of illumination in the first order between 400 and 800 nm, in the second order between 200 and 400 nm, and in the third order between 133 and 266 nm (Thompson and Walsh, 1983).

The spectrometers of both the ARL and Philips systems have a Rowland Circle configuration on a Paschen-Runge mount, the diameter of the circle being equal to the radius of curvature of the grating. As resolution increases with spectrometer size, most spectrometers have a focal length of at least 1 m. However, the ARL 34000C with focal length of 1 m can achieve comparable resolution to that of the Philips 1.5 m spectrometer, by measuring more of the shorter wavelengths in the second or third order, using its ruled grating as described above.

Precise temperature control within the spectrometer is essential, as relative movement of the grating and secondary slits caused by thermal expansion or contractions, causes peaks to be off-profile, resulting in diminished emission intensities. Spectrometer cabinet temperatures are therefore thermostatically

Figure 3.8

The optics of a scanning monochromator. The Czerny-Turner mounting of the diffraction grating is represented schematically (after Thompson and Walsh, 1983).



controlled to $\pm 0.1^{o}C$, to minimise the effect of room temperature fluctuations.

Scanning monochromators are set up at 180^{o} to the main spectrometer in both ICP-OES systems, enabling the monochromator and polychromator to view the ICP simultaneously. The use of a monochromator can introduce considerable flexibility into the system, particularly in the case of the Philips instrument. The SOPRA F400 used with the Philips PV8490 ICP is an evacuated instrument, facilitating access to the vaccuum ultraviolet region, which the main spectrometer, the air-path PV8210 cannot reach. Sulphur determinations carried out with the SOPRA monochromator are described in chapter 4. A schematic diagram of a typical Czerny-Turner monochromator is presented in figure 3.8.

Once the emission signal has stabilised, the small electrical signal generated by light falling on the photomultiplier(s) is used to charge a small microfarad capacitor. By charging the capacitor for a specified period (typically 5-15 seconds), the signal is integrated. Instrumental precision can be improved by repeating the integration. The charge on the capacitor is then discharged, converted to an electrical signal and transferred to the computer (Thompson and Walsh, 1983).

There are numerous emission lines that are available for each analyte (for example see tables by Harrison (1969) and Boumans (1983)), but usually only one is monitored. The spectral lines selected for routine analysis using the Philips and ARL spectrometers, are presented in table 3.2. There are two basic criteria for line selection, concentration range of determinand in the sample and lack of serious interferences from nearby lines. The concentration range is significant, as although ICP calibrations are linear over several orders of magnitude, calibration line curvature

Table 3.2

SPECTRAL LINES ROUTINELY USED IN THE ARL AND PHILIPS ICP SPECTROMETERS

	ARL	Philips		ARL	Philips
El.	Wavelength (nm)		El.	Wavelength (nm)	
Al	308.21	308.21	Mg	279.08	383.83
Be	313.04	313.04	Mn	257.61	257.61
B	249.68		Mo	202.03	
Ca	315.89	315.89	Na	589.00	589.00
Cd	226.50		Nd		430.36
Ce	380.15	418.66	Ni	231.60	231.60
Co	228.62	228.62	P	178.20	213.62
Cr	267.72	267.72	Pr		422.29
Cu	324.75	324.75	Sc	361.38	361.38
Dy		353.17	Si	288.16	288.16
Er		390.63	Sm		359.26
Eu	393.05	381.97	Sr	407.77	407.77
Fe	259.94	259.94	S	180.73	180.73
Gd		335.05	Ti	337.28	337.28
Ho		345.60	V	311.07	290.88
K	766.49	766.49	Y	371.03	371.03
La	398.85	398.85	Yb		328.94
Li	670.78	670.78	Zn	202.55	213.86
Lu		261.54	Zr	343.82	338.20

can be a problem at high intensities. Thus the most sensitive lines are used for elements present at low concentrations, unless subject to serious interference from other lines, rather than for major elements.

A considerable amount of research has been undertaken in the area of spectral interferences in ICP-OES (for example, Mermet and Trassy, 1981; Kempster *et al.*, 1983; Kato *et al.*, 1984; Thompson and Walsh, 1983; Boumans, 1986) as they can seriously limit the performance of ICP analysis. The three main types of spectral interference are direct spectral overlap, wing overlap and background shift. An example of direct spectral overlap where almost total coincidence of the analyte spectral lines occur is the overlap of the sensitive 180.73 nm sulphur line with a weak calcium line at 180.7 nm. This type of overlap can only be corrected for mathematically, although in the case of calcium and sulphur in groundwater samples, this is fairly easily accomplished, the concentrations of both elements being generally of the same order of magnitude.

An example of wing-overlap, significant in the analysis of groundwater samples, is that of the Mg 202.58 nm line on the Zn line at 202.55 nm. Figure 3.9a shows a scan of a preconcentrated groundwater from the Lincolnshire Limestone aquifer, with appropriate blanks. It was performed using the ARL SAMI facility described above. A slight wing overlap of the zinc line by magnesium (equivalent to 270 mg l^{-1} Mg in the sample) is observed, and is more clearly identified when the background emission is removed as in figure 3.9b.

Background shifts often give rise to spurious analyte signals during trace element analysis. Aluminium is traditionally problematic, as it emits a broad background continuum in the 190-

Figure 3.9

a) Spectral scans of a preconcentrated groundwater (containing 270 mg/l Mg) and blank solutions around the Zn line at 202.55 nm

b) The same scan after the background emission has been subtracted, demonstrating the strong wing-overlap of Mg (202.58 nm) on the Zn line

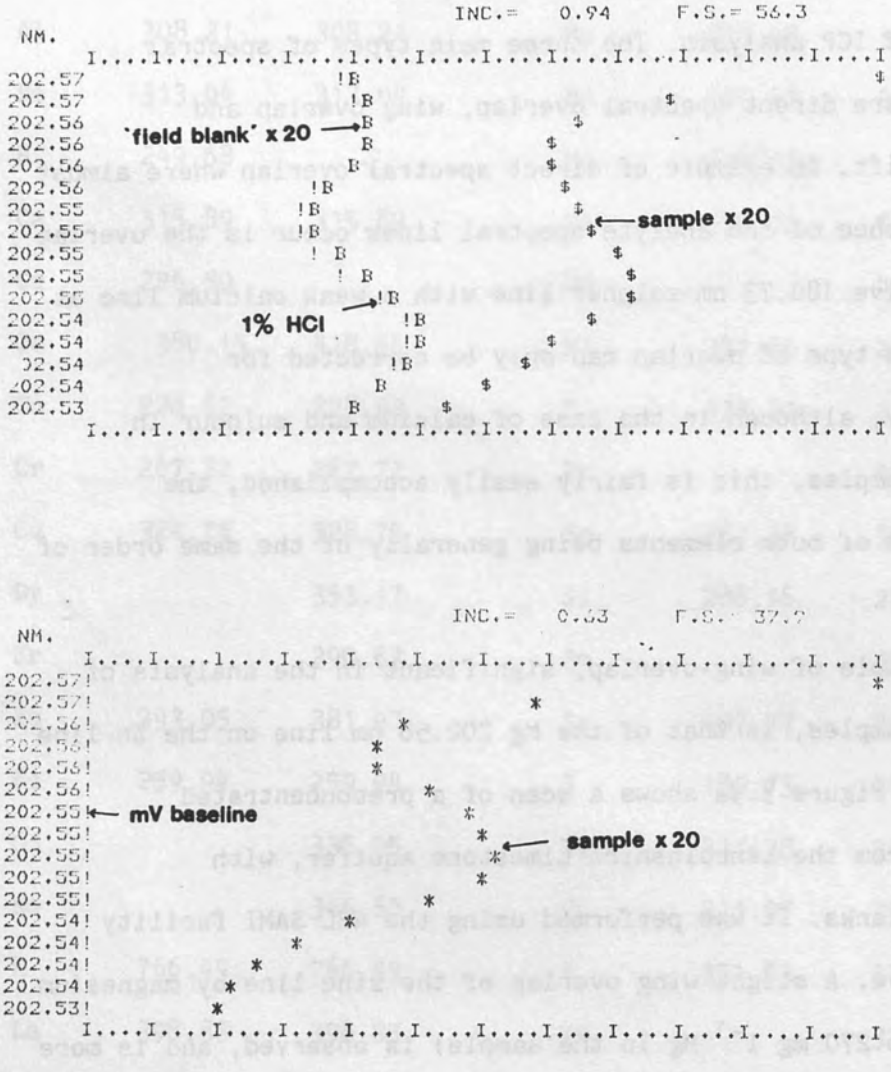
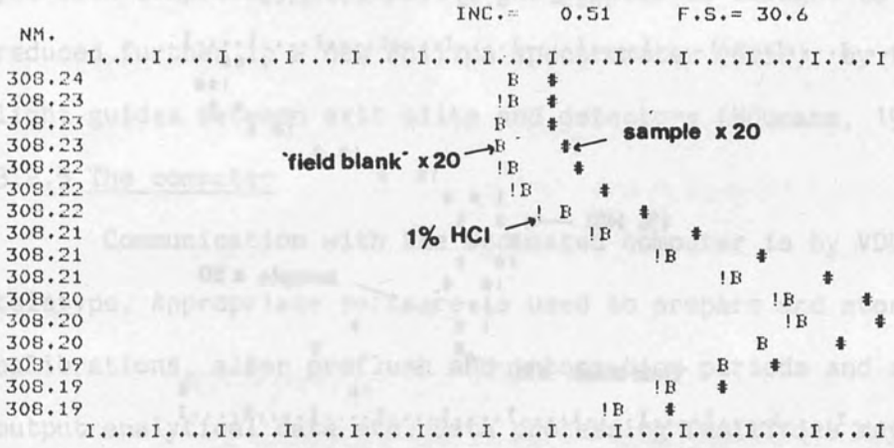


Figure 3.10

a) Spectral scan of a preconcentrated groundwater and blank solutions around the Al line at 308.2 nm. Background shift obscures the analyte peak.

b) The same scan after the background emission has been subtracted to reveal the actual Al peak (approximately 1.6 mV)



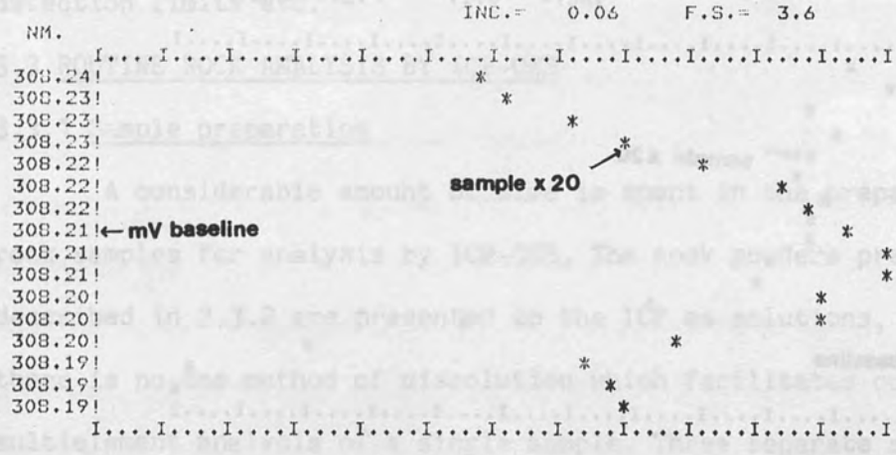
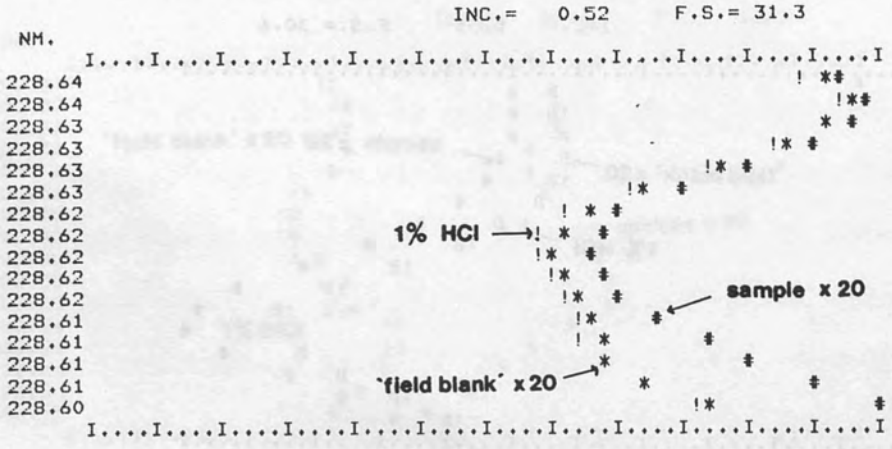
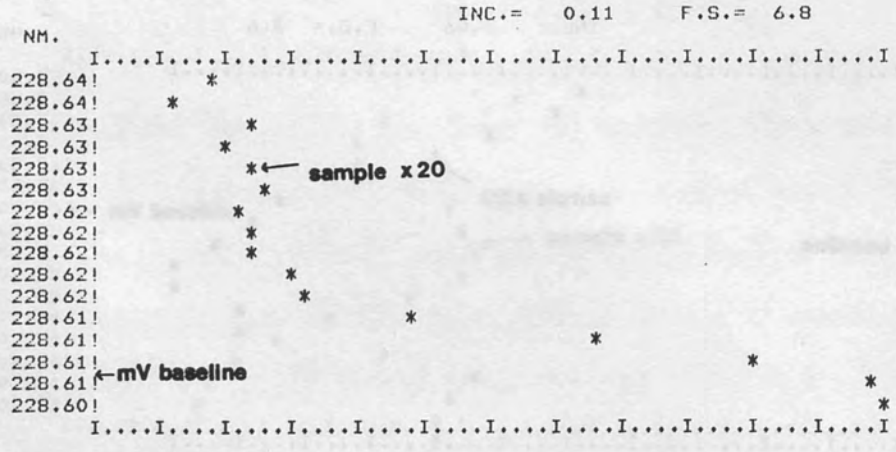


Figure 3.11

a) Spectral scans of a preconcentrated groundwater and blank solutions around the Co line at 228.62 nm.

b) The same scan with the background emission removed. No quantifiable cobalt peak is apparent.





220 nm range, enhancing the background signal beneath analyte peaks at these wavelengths. Slight background shift is demonstrated in scans of two other preconcentrated groundwaters in figures 3.10a and 3.11a. When background emission is removed, a small analyte peak for aluminium is identified (figure 3.10b), whereas no cobalt is present in figure 3.11b.

Another form of interference is that caused by stray light, which, despite great improvements in spectrometer design, has not yet been completely eradicated. The problem is thought to have been reduced further in a new Philips spectrometer (8050), by the use of light guides between exit slits and detectors (Boumans, 1986).

3.2.5 The computer

Communication with the dedicated computer is by VDU or teletype. Appropriate software is used to prepare and store calibrations, alter preflush and integration periods and store and output analytical data etc. Data processing facilities may also be available to perform background corrections and assist in the calculation of spectral interferences, correction coefficients, detection limits etc.

3.3 ROUTINE ROCK ANALYSIS BY ICP-OES

3.3.1 Sample preparation

A considerable amount of time is spent in the preparation of rock samples for analysis by ICP-OES. The rock powders prepared as described in 2.3.2 are presented to the ICP as solutions, however there is no one method of dissolution which facilitates complete multielement analysis of a single sample. Three separate solutions are therefore prepared for the determination of major, trace and rare earth elements in silicate rocks. The techniques are summarised below; details of the methodologies are presented in chapter 4 of Thompson and Walsh (1983).

Solutions for trace element analysis are prepared by acid-digestion. Rock powder is evaporated to dryness with a 4:1 $HF/HClO_4$ mixture, the residue taken up in concentrated HCl and the solution made up to a final volume representing a 100-times dilution of the rock sample. Some major elements may be determined in this solution in addition to the trace elements: Ba, Ce, Co, Cr, Cu, La, Li, Nb, Ni, Sc, V, Y and Zn. However silicon is lost during the evaporation process and certain accessory minerals are not completely attacked by the acid-digestion. Elements such as zirconium and others which are concentrated in tourmaline, beryl, rutile, chromite, pyrite, cassiterite, kyanite and the spinels, (Thompson, 1985) for example, cannot be reliably determined in the "trace element solution".

A more powerful whole-rock attack is acheived using a lithium metaborate fusion. Rock powder and $LiBO_2$ in a 1:3 ratio, are fused in a platinum crucible over a meker burner and the fusion bead dissolved in 5% v/v HNO_3. The original dilution factor of 500 has been increased recently to 2000 to improve instrumental precision; this solution is therefore too dilute for the determination of most trace elements. The success of the $LiBO_2$ fusion was demonstrated by Suhr and Ingamells (1966) and Burman *et al.* (1978). Fusion with $LiBO_2$ allows the simultaneous determination of all the major elements (Si, Al, Fe, Mg, Ca, Na, K, Ti and Mn) in one solution, which is not possible when alternative fluxes such as Na_2CO_3 or KOH are employed. While the use of $LiBO_2$ precludes the determination of lithium, it is easily determined in the less dilute "trace element solution", produced by the acid-digestion method. Due to the low abundance of most elements in the Lincolnshire Limestone samples, in comparison with the silicate rocks, the "major element solutions" were only appropriate for silicon and calcium determinations.

A third solution is prepared for the determination of rare

earth elements (REEs), the preparation involves preconcentration on a cation exchange column and results in an overall dilution of the rock sample by a factor of just ten. The rock powder is digested by the $HF/HClO_4$ method and filtered. If the presence of resistant accessory minerals is suspected, a mini-fusion of the residue and filter-paper is carried out, the ash dissolved in HCl and this solution added to the filtrate. The sample solution is diluted and loaded onto a 12 cm column of 200-400 mesh DOWEX AG-50W-X8 resin. The column is eluted with 450 ml of 1.7M HCl to remove most major and minor elements and this portion of solution discarded. The REEs and a small quantity of scandium and strontium are eluted from the resin with 600 ml of 4M HCl; this portion is evaporated to dryness and then redissolved in 5 ml HNO_3 prior to analysis.

Appropriate blanks and standards are prepared by each method to reduce the problems caused by matrix interferences, i.e., the sample, standard and blank solutions are prepared with identical viscosities, acidities etc. Compatability is of great significance, as matrix effects are known to affect the excitation characteristics of the ICP (Thompson *et al.*, 1982a; Ramsey and Thompson, 1986). In-house standards are used for calibration and drift correction, "standard" rocks for checking the accuracy of the determinations. The three routinely used calibration standards are igneous rock mixtures, therefore a synthetic $CaCO_3$ standard (equivalent to 56% CaO) was also prepared, being more appropriate to the analysis of the Lincolnshire Limestone samples. Rare earth element calibration standards were prepared from synthetic reagents.

3.3.2 Analysis

The three groups of solutions prepared for analysis by ICP-OES vary considerably, having different matrices, concentration ranges and groups of determinands. The solutions are therefore

Table 3.3

OPERATING CONDITIONS FOR ROUTINE ROCK ANALYSIS ON THE PHILIPS ICP-OES INSTRUMENT

PARAMETER	ROCK ANALYSIS PROGRAM		
	Major Element	Trace Element	REE
Argon flow rates (l min^{-1})			
Coolant	11	11	11
Auxilliary	2	1	0 - 0.5
Carrier	9	8.5	9
Power settings			
Phase Voltage (V)	155	150	150
Anode Current (A)	0.44	0.41	0.39
Grid Current (A)	0.15	0.137	0.135
Observation height	12-16 mm above load coil		

analysed using separate programs, each requiring a different set of operating conditions namely high voltage and power settings and gas flow rates.

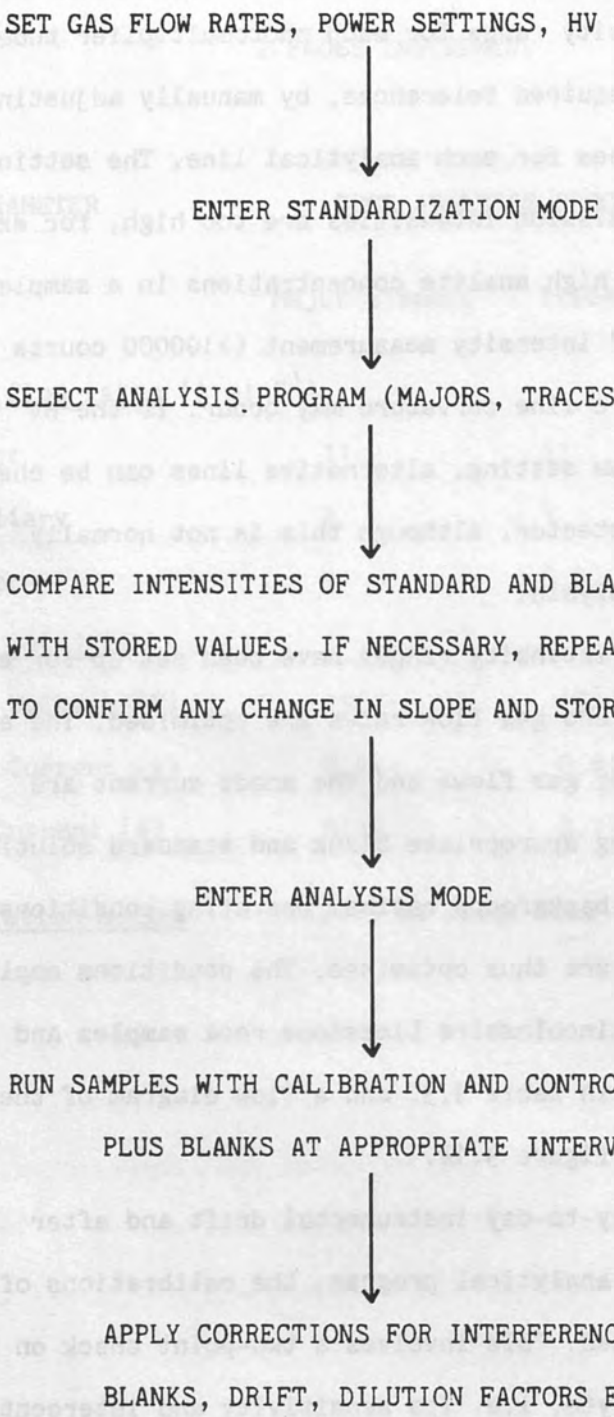
The normal intensity range for each photomultiplier tube is maintained within the required tolerances, by manually adjusting the high voltage (HV) switches for each analytical line. The settings can be reduced if the emission intensities are too high, for example if there is a danger of high analyte concentrations in a sample producing an "off-scale" intensity measurement (>100000 counts per second) or in cases where line curvature may occur. If the HV control is at its minimum setting, alternative lines can be checked using the roving slit detector, although this is not normally necessary in routine analysis.

Once appropriate intensity ranges have been set up for each analyte, power settings and gas flow rates are optimised. The effect of auxilliary and carrier gas flows and the anode current are investigated by analysing appropriate blank and standard solutions and comparing signal to background ratios. Operating conditions for each analytical program are thus optimised. The conditions employed during the analysis of Lincolnshire Limestone rock samples and residues, are presented in table 3.3. and a flow diagram of the analytical procedure in figure 3.12.

To correct for day-to-day instrumental drift and after changing to a different analytical program, the calibrations of each program are restandardized. This involves a two-point check on the calibration of each analyte, i.e. its sensitivity and intercept, using the appropriate reagent blank and rock standards respectively. The quality of the analytical data are further improved by normalisation to within-batch standards, and the accuracy checked by the occasional inclusion of certified reference materials.

Figure 3.12

Flow diagram of the analytical procedure for the Philips ICP-OES system



Analysis time for each sample is less than one minute, with a preflush period of forty-five seconds and a single integration period of ten seconds. Major element concentrations are reported as oxides, on a weight percent (10000 ppm) basis, trace elements as ppm (mg kg^{-1}).

A few elements cause particular problems in silicate analysis, for example certain commonly used iron lines exhibit line curvature at extreme concentrations and aluminium limits the detection of certain analytes measured at low wavelengths, causing a broad spectral response below 220 nm. In limestones, calcium causes stray light problems, spectral overlap and some background enhancement. Appropriate corrections are applied as necessary.

3.4 ROUTINE WATER ANALYSIS BY ICP-OES

Many of the problems inherent in silicate analysis are not encountered during water analysis, due to the fact that samples are already in an ideal form for presentation to the ICP. The solutions are also usually more dilute, and problem elements such as iron and aluminium, which cause spectral interferences in silicate analysis, are present at very much lower concentrations. Matrix-matching between standards and samples is relatively straightforward. Samples are acidified with HCl to 1% v/v in the field (2.2.2), synthetic standards are similarly acidified during their preparation.

In silicate dissolution, the fusion method introduces additional quantities of certain analytes which precludes their determination in the sample solution. As the only chemical added to water samples is high-purity acid, a complete multielement analysis can theoretically be performed on a single sample. In practice, a preconcentration step is frequently required to increase the concentrations of various trace elements to more appropriate levels.

Table 3.4

OPERATING CONDITIONS FOR ROUTINE GROUNDWATER ANALYSIS ON THE ARL 34000C ICP SYSTEM

Gas flow rates (l min^{-1})

Coolant	11
Auxillary	1.2
Carrier	1
Argon purge	1.5

Power generator

Forward power	1080 W
Reflected power	5W

Power amplifier

Voltage	4000 V
Filament voltage	7.5 V
Grid current	0.4 A

Observation height above coil: 15 mm

3.4.1 Sample preparation

Preconcentration of water samples is frequently necessary prior to the analysis of waters for trace elements. One litre samples are concentrated twenty-times by evaporation in a laboratory at Wallingford which incorporates many of the features recommended by Moody (1982). Every precaution is taken to minimise contamination through air or container contact. The water samples are contained in PTFE beakers pre-leached in 10% AristaR HCl and the evaporation is carried out under infra-red lamps and below laminar flow hoods, in an area which can be screened off from the rest of the laboratory. The use of metal in the area of the hoods is restricted, with wooden clamps, for example, being used to support the lamps. The air to the laboratory is filtered to reduce the risk of contamination by particulate matter, and there are dust mats at the door, which is kept closed except for access.

3.4.2 Groundwater analysis

Due to the linearity of the ICP calibrations over several orders of magnitude, both preconcentrated and dilute samples are analysed using the same calibrations, therefore only a single analytical program is required. The suite of multielement standards prepared from spectroscopically pure reagents are divided into four groups: Si; SO_4 and P; major ions - Na, K, Ca, Mg, B, Li; trace elements - Sr, Ba, Be, V, Y, Fe, Cu, Mn, Co, Zn, Cd, Al, Mo, Ni, Pb. These standards are used to prepare calibrations and are also run at appropriate intervals throughout an analysis with the blank (1% HCl), to allow corrections for within-batch drift to be applied.

The operating conditions used during the analysis of the Lincolnshire Limestone groundwaters are presented in table 3.4.

Although elements such as iron and aluminium, which cause spectral overlaps in silicate analysis are present only at very low

Table 3.5

SUMMARY OF METHODS FOR ANION DETERMINATIONS BY AUTOANALYSER

Method	BROMIDE	IODINE (total)	CHLORIDE	NITRATE
Principle	Br has a catalytic effect on oxidation of iodine -> iodate by $KMnO_4$ in H_2SO_4 soln. ↓ unreacted I is extracted in CCl_4 and determined	iodate ↓ arsenious acid ↓ iodine then, iodate-I catalyses reaction: ↓ arsenious acid + Ce (IV) sulphate	mercuric thiocyanate + Cl ions ↓ thiocyanate ions + $HgCl_2$ ↓ thiocyanate ion + Fe^{3+} ions ↓ coloured ferric thiocyanate soln.	NO_3 -> NO_2 via Cd-Cu reduction column ↓ nitrite ions + sulphanil-amide ↓ diazo compound ↓ diazo comp. + N(1-naphthyl) -ethylene-diamine-di-hydrochloride ↓ reddish azo dye
Absorbance/ Transmission	Abs. (inverse)	Trans.	Abs.	Abs.
Colorimeter Filter:	520 nm	410 nm	480 nm	520 nm
Flow cell:	50 mm	15 mm	15 mm	59 mm
Calibration range	0 - 10 µg/l	0-5 µg/l 0-100 µg/l	0-50 mg/l 25-250 mg/l	0-2 mg/l NO_3-N
Detection limit	1.3 µg/l	0.1 µg/l	500 µg/l	10 µg/l
References	Andrews, (1982) Pyen *et al.*, (1980) Moxon & Dixon, (1980)	Jones, (1982) Truesdale, (1975)	Feldkamp *et al.*, (1974) Zall *et al.*, (1956)	Cook & Miles (1980); Nydahl (1976); Stainton (1974); Henriksen (1965); Morris & Riley (1980)

levels, other elements such as calcium and magnesium interfere by causing background enhancement and line overlap etc. The identification of such interferences is relatively straightforward using the SAMI facility described in 3.2.4. Examples of corrections applied to correct spectral interferences in the Lincolnshire Limestone groundwaters include: Ca on SO_4, Y, Si, Sc and La; Mg on Mn, Fe, Zn, Cr and Si; Fe on V, Zn, Cd and Zr.

3.5 NON-ICP-OES TECHNIQUES USED IN ROUTINE GEOCHEMICAL ANALYSIS

The clay mineralogy of argillaceous Lincolnshire Limestone samples and major phases of the groundwater residues (4.5) were investigated by XRD. Oriented specimens of the non-carbonate portion of the limestones were prepared by suction of the suspended material onto an unglazed ceramic disk (Shaw, 1972); randomly oriented specimens were affixed to a glass slide with acetone. A Philips PW1720 diffractometer was used, with power settings at 40 kV and 25 mA, and employing a Co target and Fe filter.

Scandium and lead were determined in the groundwater residues, and rubidium was determined in both the residue and limestone sample sets, by AAS. A Pye Unicam PU9000 instrument, incorporating double-beam optics, was used to analyse the "trace element solutions", prepared by acid-digestion (3.3.2).

3.6 NON-ICP-OES TECHNIQUES USED IN ROUTINE GROUNDWATER ANALYSIS

Automated colorimetric and spectrophotometric determinations of total iodine, bromide and nitrate, were carried out using a Technicon II autoanalyser. Details of the operating conditions and principles of the chemistry for each method are summarised in table 3.5.

The bicarbonate ion concentration of groundwaters was determined at the time of sampling using a digital titrator. Dilute sulphuric acid was titrated against the water sample, using

Table 3.6

ION-SELECTIVE ELECTRODE METHOD FOR FLUORIDE AND SULPHIDE DETERMINATIONS IN GROUNDWATER SAMPLES

	Fluoride ISE	Sulphide ISE
BUFFER		
name	TISAB Total Ion Strength Adjustment Buffer	SAOB Sulphide Anti-Oxidant Buffer
reagents	in 500 ml: 57 g glacial acetic acid 58 g NaCl, 4 g CDTA NaOH to adjust pH to 5 - 5.5	10 M KOH 0.1 M ascorbic acid
dilution buffer/sample	50:50	50:50
purpose	swamps matrix effects- pH & ionic strength	swamps pH changes (0.1 pH ---> 20% error)
precautions	Measure all samples approximately & arrange in ascending order of concentration to reduce electrode response time. Check temperature	To prevent oxidation of SAOB: Purge containers with N_2 Store solutions under N_2 Store in dark Maintain constant temperature
Nernst response	58 mV, negative slope	29.5 mV, positive slope
Calibration range	0.1 - 10 mg l^{-1}	0.1 - 500 mg l^{-1}
References	Frant & Ross, 1968 Rix & Smith, 1976	Gulens, 1985

bromocresol-green, as the titration end-point indicator (2.2.2.2). On return to the laboratory, the on-site measurements were checked with an Orion autotitrator, which monitors pH throughout the titration of standard sulphuric acid against the sample.

Fluoride and sulphide ions were determined using ion-selective electrodes (ISEs). Details of each method are presented in table 3.6. The use of the sulphide ISE is discussed in section 4.2.3.

CHAPTER FOUR

4: ICP-OES APPLICATIONS, PRECISION AND DETECTION LIMITS

4.1 INTRODUCTION

Several new adaptations of ICP-OES techniques have been developed using both the ARL and Philips systems. Dissolved sulphide was successfully determined in groundwaters using a gas liquid separator, and a novel preconcentration technique facilitating the determination of rare earth elements in the Lincolnshire Limestone groundwaters was developed. The method involved the total evaporation of the water samples to a residue with subsequent dissolution by standard rock-dissolution methods and analysis by ICP-OES. Sulphate-sulphur was also determined in the residues using the vacuum monochromator in conjunction with the Philips instrument. An analytical program was set up on the same system to facilitate the direct determination of major elements in groundwaters. The precision and detection limits of the two instruments are evaluated and data valid under routine analytical conditions rather than ideal, short-term conditions, are presented.

4.2 DETERMINATION OF DISSOLVED SULPHIDE IN GROUNDWATERS BY ICP-OES

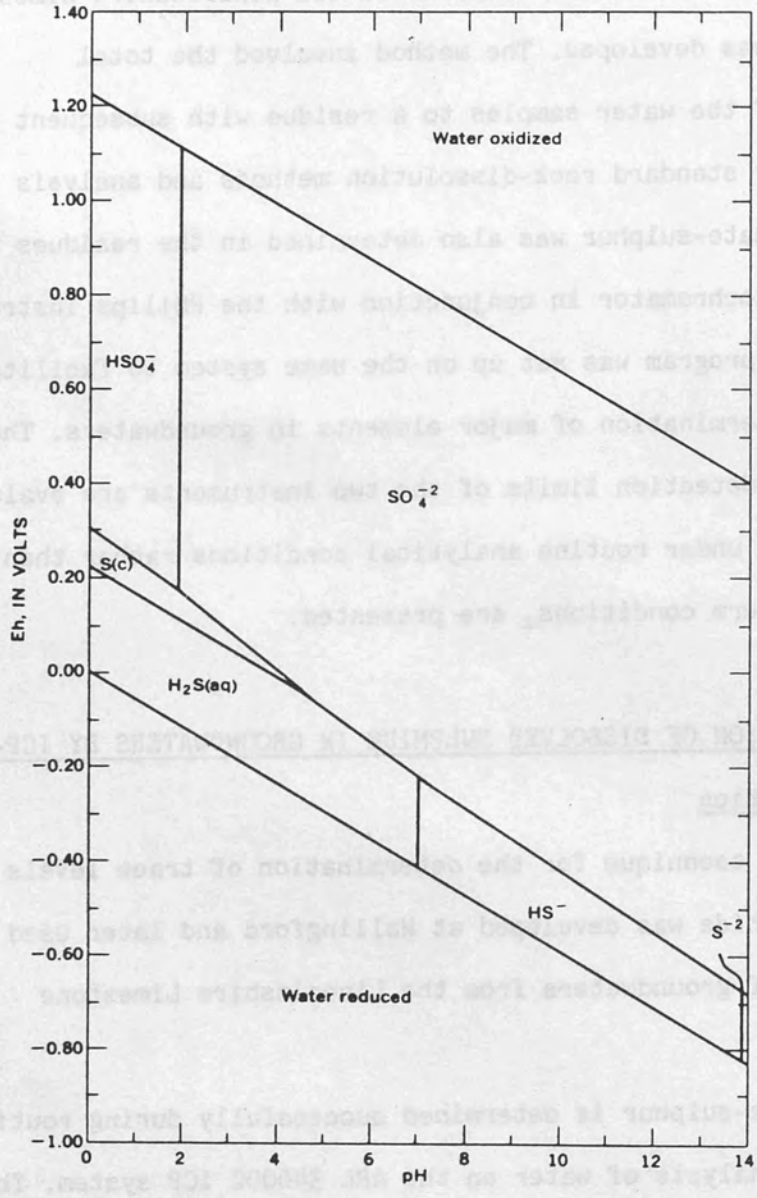
4.2.1 Introduction

A novel technique for the determination of trace levels of dissolved sulphide was developed at Wallingford and later used for the analysis of groundwaters from the Lincolnshire Limestone aquifer.

Sulphate-sulphur is determined successfully during routine multielement analysis of water on the ARL 34000C ICP system. The 180.73 nm sulphur line is used, with the light-path between the plasma and spectrometer purged with argon to minimise absorption (Miles and Cook, 1982). The only serious interference is from a

Figure 4.1

Stability fields of sulphur species at equilibrium at 25°C and 1 atmosphere pressure. Total dissolved sulphur activity is 96 mg l^{-1} as SO_4^{2-} (Hem, 1970)



nearby weak calcium line, for which a correction may be made.

For many groundwaters, the redox conditions are such that sulphur is in the oxidised form, that is, the sulphate ion is predominant. However, under certain reducing conditions, HS^- and dissolved H_2S can occur (figure 4.1). During repeat analyses of groundwaters from the the Lincolnshire Limestone aquifer, a progressive decrease in apparent sulphate-sulphur concentrations was observed. It was suspected that the initial high apparent sulphur concentrations were due to enhancement of the signal by the liberation of hydrogen sulphide from solution during nebulisation. Continued volatilisation during repeat analyses therefore resulted in decreasing apparent sulphur concentrations. Initial experiments suggested that this phenomenon could be used as the basis of a method for the determination of low concentrations of dissolved sulphide. Following a series of experiments to optimise the technique, dissolved sulphide was determined in groundwater samples from the Lincolnshire Limestone by this method.

The determination of dissolved, reduced species such as sulphide in groundwaters, is desirable as it provides information on the redox conditions prevailing in the aquifer. Such conditions influence the release and mobility of many elements including some which are potentially toxic (Champ *et al.*, 1979; Edmunds *et al.*, 1984). The limitations of Eh measurements using a platinum electrode are well known and provide only a qualitative guide to the overall redox state of the water (Whitfield, 1974; Lindberg and Runnels, 1984).

Several techniques for sulphide determination have been described, including colorimetry (Rees *et al.*, 1971), titrimetry (DoE, 1983), atomic fluorescence spectrometry (Shahwan and Heithmar, 1984), ion chromatography (Rocklin and Johnson, 1983) and the

Figure 4.2

Gas-liquid separator

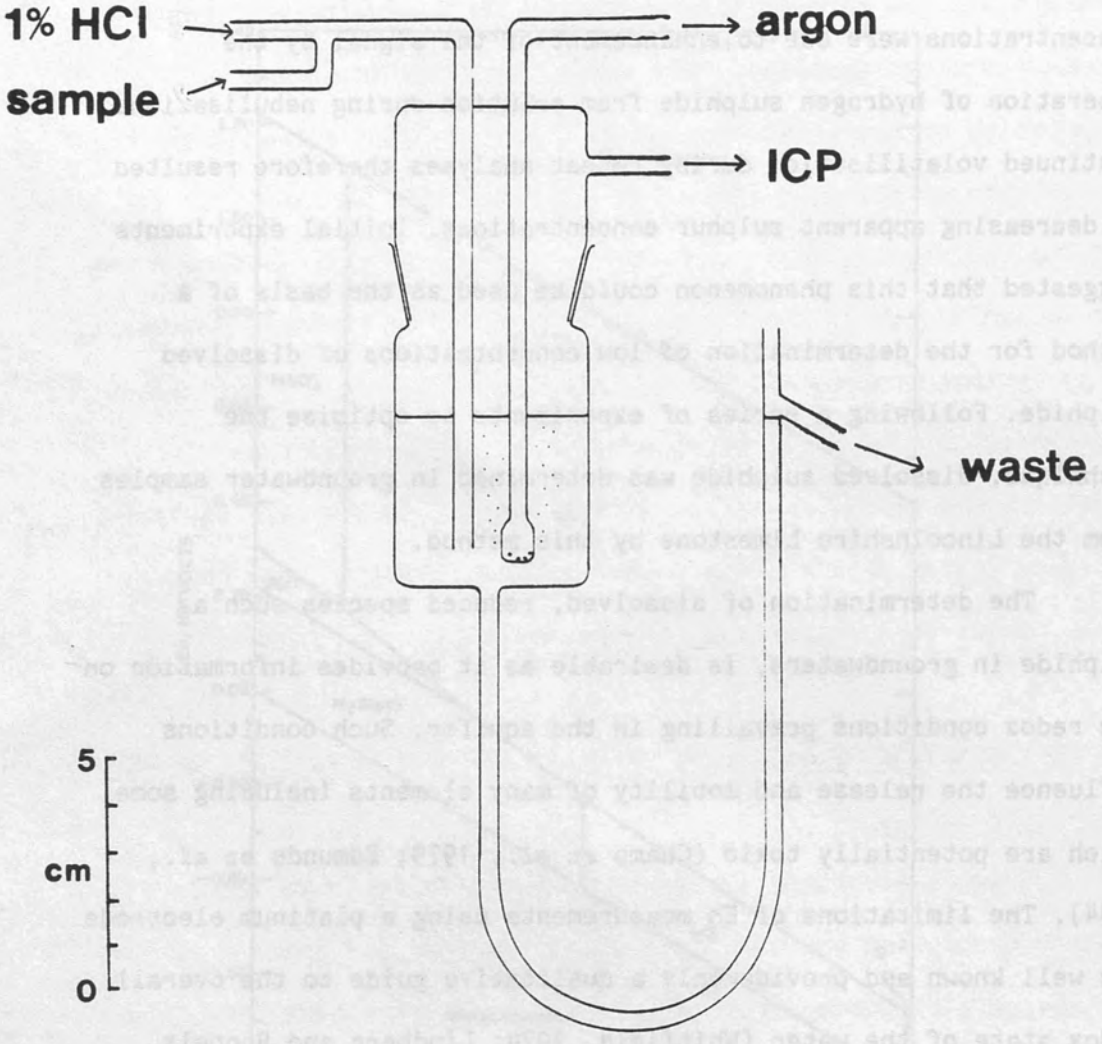
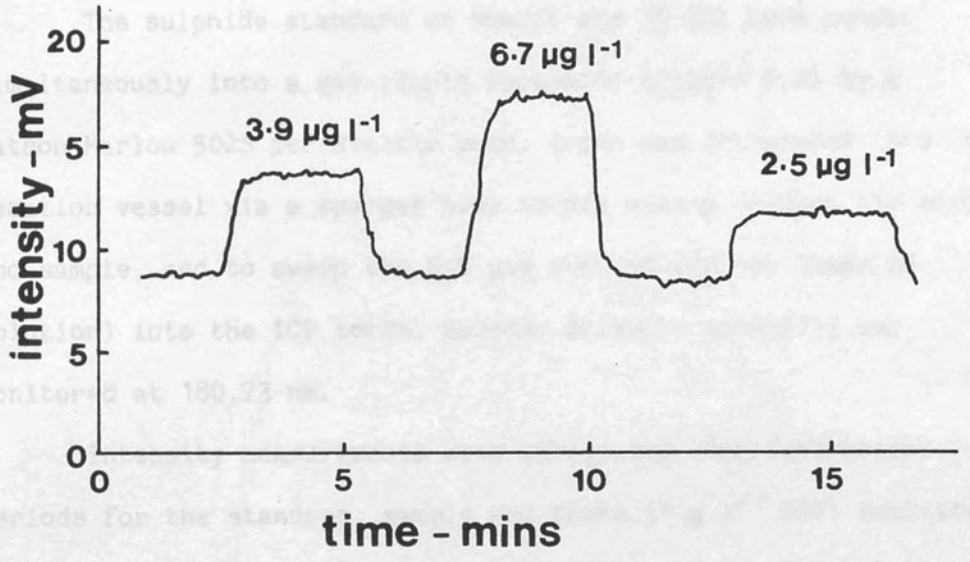


Figure 4.3

Plot of emission intensities at 180.7 nm during dissolved sulphide determinations. Three groundwaters containing trace amounts of sulphide are aspirated alternately with a blank solution.



sulphide ion-selective electrode (Gulens, 1985), all of which have limitations in terms of speed, sensitivity and interference effects. A comparison of the ICP-OES and ion-selective electrode methods are described in 4.2.3.4.

4.2.2 Method

A stock sulphide standard was prepared from $Na_2S.9H_2O$, standardised against 0.1M $AgNO_3$ and diluted daily to provide a series of working standards in the range 0.1-100 µg l^{-1}. In order to prevent the loss of sulphur from solution as hydrogen sulphide gas, all standard solutions and samples were adjusted to a pH of 11.5-12 by the addition of KOH, to give a concentration of 1 g l^{-1}.

The sulphide standard or sample and 1% HCl were pumped simultaneously into a gas-liquid separator (figure 4.2) by a Watson-Marlow 502S peristaltic pump. Argon was introduced into the reaction vessel via a sparger head to aid mixing between the acid and sample, and to sweep the H_2S gas evolved (in the lower pH solution) into the ICP torch. Sulphur emission intensity was monitored at 180.73 nm.

Intensity measurements were integrated over five second periods for the standard, sample and blank (1 g l^{-1} KOH) solutions, and the measurements plotted manually (figure 4.3). The calibration was linear over four orders of magnitude; however, at high sulphur emission intensities (ie. greater than 1000 mV, which is equivalent to a concentration of 1 mg l^{-1} sulphide), the signal took a long time to stabilise. A calibration range of 0.1-100 µg l^{-1} was therefore selected for normal analysis.

4.2.3 Results

4.2.3.1 Optimisation

Various instrumental parameters which influenced the sensitivity of the technique were investigated. Increased

Figure 4.4

Effect of liquid flow rate on the emission intensity of 2 μg l^{-1} of sulphide at an argon flow rate of 0.35 l min^{-1}

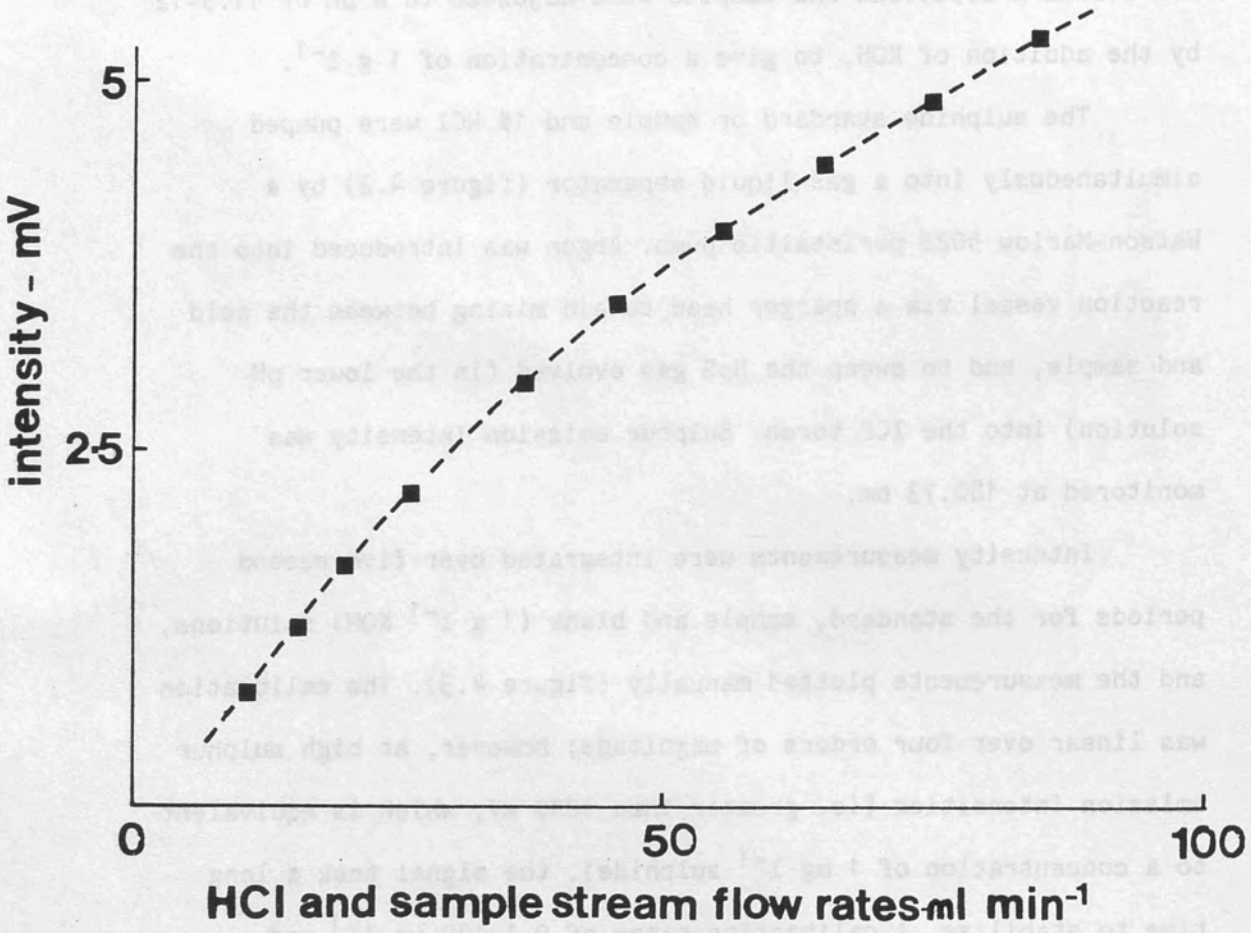
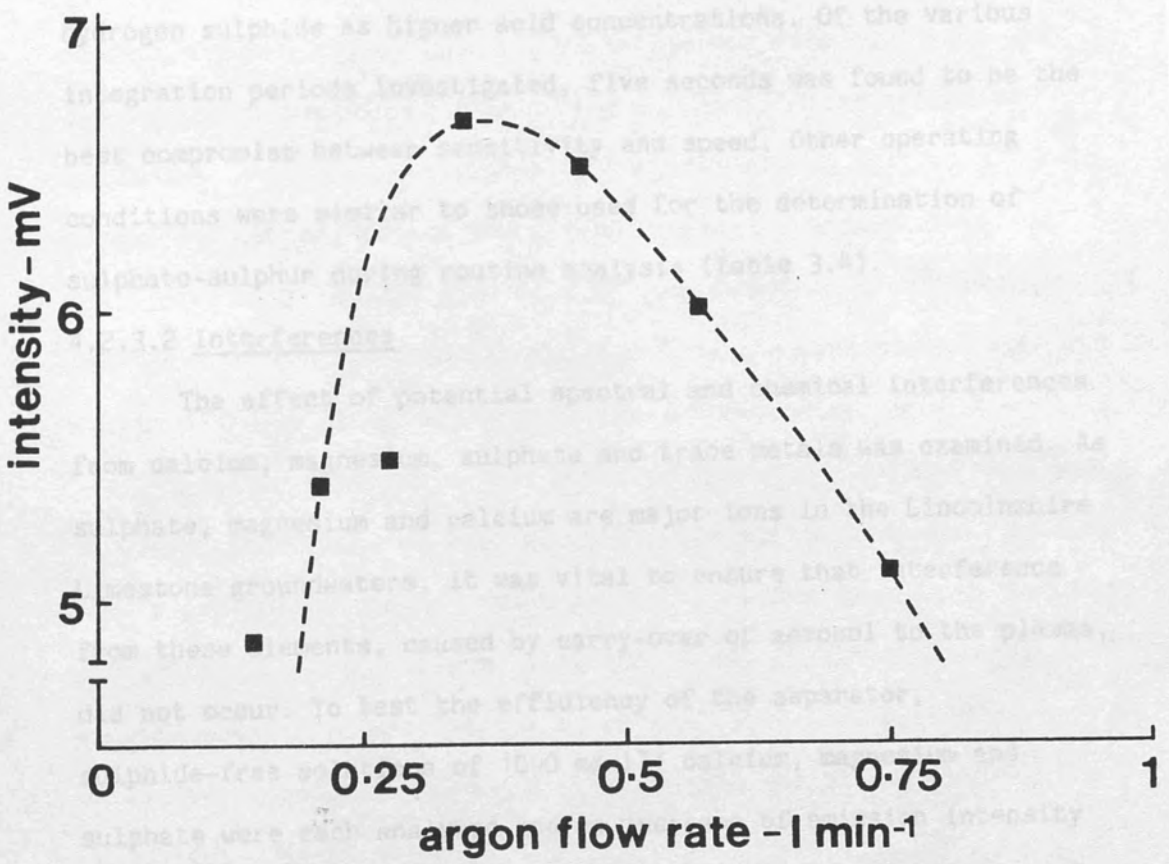


Figure 4.5

Effect of argon flow rate on the emission intensity of 5 µg l^{-1} sulphide at a liquid flow rate of 25 ml min^{-1} for both HCl and sulphide solutions



sensitivity was obtained at high liquid flow rates (figure 4.4), however a flow rate of 25 ml min^{-1} for both the HCl and sample streams was selected for routine use to minimise reagent and sample consumption. At low argon flow rates, slow mixing of the acid and sample in the gas-liquid separator and inefficient stripping of H_2S resulted in low emission intensities, whereas high gas flow rates forced liquid out of the vessel prematurely. At a liquid flow rate of 25 ml min^{-1} per stream, a gas flow rate of 0.35 l min^{-1} was found to be the best compromise (figure 4.5).

A hydrochloric acid strength of 1% was selected to decrease the pH of the test solution, as it was as efficient at releasing hydrogen sulphide as higher acid concentrations. Of the various integration periods investigated, five seconds was found to be the best compromise between sensitivity and speed. Other operating conditions were similar to those used for the determination of sulphate-sulphur during routine analysis (table 3.4).

4.2.3.2 Interferences

The effect of potential spectral and chemical interferences from calcium, magnesium, sulphate and trace metals was examined. As sulphate, magnesium and calcium are major ions in the Lincolnshire Limestone groundwaters, it was vital to ensure that interference from these elements, caused by carry-over of aerosol to the plasma, did not occur. To test the efficiency of the separator, sulphide-free solutions of 1000 mg l^{-1} calcium, magnesium and sulphate were each analysed and no increase of emission intensity above background was recorded, demonstrating the insensitivity of the method to sulphate-sulphur and the lack of any interference caused by line-overlap or background shift from calcium and magnesium.

The potential interference caused by several metals present

in groundwaters at trace levels was investigated by spiking 10 μg l^{-1} sulphide solutions with ferrous and ferric iron, zinc, copper and aluminium in the range 0.1-100 mg l^{-1}. Iron and zinc did not interfere, but the higher concentrations of aluminium depressed the sulphide emission intensity, and copper caused immediate precipitation of sulphide as CuS. However, in natural groundwaters with trace metals present at the μg l^{-1} level and in equilibrium with any sulphide minerals present, free dissolved sulphide would still be liberated and such interferences would be insignificant.

4.2.3.3 Precision and detection limit

The precision, detection limit and background equivalent concentration (defined in 4.6), of the method were evaluated and compared with the performance of the sulphide ion-selective electrode. Twenty repeat intensity measurements of a 10 μg l^{-1} sulphide standard, gave a short-term relative standard deviation (RSD) of 0.45%, the RSD rose to 2.5% when measured over a working week. A 3σ detection limit calculated from the background noise was 0.2 μg l^{-1}; the background equivalent concentration was 6.7 μg l^{-1}.

Similar performance was achieved when the separator was used in conjunction with the Philips PV8490 ICP system at Egham. A SOPRA F400 argon-purged vacuum scanning monochromator was used to monitor the sulphur emission intensity at 180.73 nm. Replicate intensity measurements on several standards gave RSDs of 0.5-1%, the 3σ detection limit obtained was 0.5 μg l^{-1} and the background equivalent concentration 7.7 μg l^{-1}.

4.2.3.4 Comparison of the method with measurement by sulphide ISE

The performance of the sulphide technique described above was compared with that of the silver-sulphide ion-selective electrode. Additional precautions were required when using the ISE, to prevent the loss of sulphide from solution (see 3.6). All samples and

Table 4.1

COMPARISON OF THE ICP-OES AND ISE SULPHIDE METHODS

	ICP-OES	ISE
Calibration	0.1-1500 µg l^{-1}	10-10000 µg l^{-1}
Optimum range	0.5-75 µg l^{-1}	>50 µg l^{-1}
Analysis time	1-3 mins	1-10 mins
pH buffer	1 g l-1 KOH	SAOB
3s detection limit	0.2 µg l^{-1}	49 µg l^{-1}
Analytical precision	0.5-2% RSD	0.5-5% RSD
Correlation coefficient (n = 50)	0.97	

standards were diluted 50:50 with sulphide anti-oxidant buffer (SAOB), which is essentially 10N KOH (to maintain a high pH and swamp any effects from sample pH or ionic strength) and ascorbic acid (a reducing agent). The SAOB was itself protected from oxidation by using degassed water in its preparation, purging all flasks and bottles with oxygen-free nitrogen, storing all solutions under nitrogen and in the dark, and keeping the storage period as short as possible.

The ISE was used in conjunction with an Orion pH/mV meter. The samples were determined by both methods simultaneously, but due to the electrode's slow response and the amount of time required to prepare each sample and standard solution for ISE determination, only 15 samples could be analysed daily. The analysis of 50 Lincolnshire Limestone groundwaters was therefore carried out over four consecutive days.

Reasonable agreement was obtained between the two sets of sulphide results. No systematic bias was identified and a high positive correlation was obtained; the correlation coefficient for the 50 samples being 0.97.

The overall precision of the methods was tested by analysing 10 replicate samples of Lincolnshire Limestone groundwater. The mean sulphide concentration was 85 $\mu g\ l^{-1}$ and the RSD of the concentrations obtained was 5% for the ICP method and 17% for the ISE. A comparison of the ICP and ISE method is summarised in table 4.1.

4.2.4 Conclusion

The ICP-OES method for determining sulphide in groundwaters is rapid and simple. In comparison with the ion-selective electrode it is very quick (average analysis time being three minutes) and sample preparation is less tedious, precision and detection limits

are also superior. Response time for the ISE method increases with decreasing sulphide concentration, while ICP response time becomes greater at higher concentrations. The new method is therefore most suitable for trace level determination of sulphide in the 0.1-75 $\mu g\ l^{-1}$ range, whereas the ion-selective electrode method is more suited to concentrations in excess of 75 $\mu g\ l^{-1}$.

Details of the new ICP-OES technique are summarised in Lewin *et al.* (1987); sulphide measurements on the groundwater samples are discussed in chapters 5 and 6.

4.3 GROUNDWATER PRECONCENTRATION BY TOTAL EVAPORATION TO A SOLID RESIDUE AND SUBSEQUENT ANALYSIS BY ICP-OES

4.3.1 Introduction

Inductively-coupled plasma optical emission spectrometry is a rapid and sensitive technique, facilitating simultaneous, multielement analysis of geochemical samples down to the $mg\ kg^{-1}$ level. For routine rock analysis direct determination on the digest is usually adequate. However, groundwaters are very much more dilute solutions, with many elements occurring at the $\mu g\ l^{-1}$ level or below. A preconcentration step is frequently required to raise the trace element concentrations to ranges in which they can be determined.

A brief review of techniques commonly used to preconcentrate water samples is presented and a novel preconcentration method for the groundwaters from the Lincolnshire Limestone aquifer is described.

4.3.2 Preconcentration techniques for trace element determinations in natural waters

Numerous preconcentration techniques for the trace element analysis of waters have been reported. They can be separated into

two basic categories: selective, when particular analytes are concentrated and the rest discarded; and non-selective, when all solutes are equally preconcentrated (Thompson and Walsh, 1983). Selective techniques such as ion-exchange and solvent extraction have been widely used for the trace element analysis of seawater, facilitating the reliable determination of metals at the ng l^{-1} to µg l^{-1} level in a salt-free matrix.

During all stages of the treatment of water samples for trace element analysis, (sampling, storage, preparation etc.), particular care is required to avoid contamination. Ultimately, practical detection limits are frequently determined by levels of analytes in the blanks.

4.3.2.1 Ion exchange resins

Ion exchange resins contain fixed charge-carrying groups and mobile counter ions of the opposite charge. As a solute passes through the resin, the counter ions are reversibly exchanged for those in the solute carrying a like charge. The most widely used resins are styrene and divinyl benzene co-polymers produced in a bead form. By control of the polymerization process, the resin produced can be made gel-like (microreticular), with pores comparable to the size of inorganic or small organic ions, or as a more open structure in which pores are tens of nanometres in diameter. The cation or anion exchanging properties are introduced into the resin by chemical modification after polymerization. Cation exchangers, those most commonly used in the preconcentration of water samples, are either strong-acid types containing SO_3H groups, or weak acid types containing COOH groups.

Resins can be prepared with chelating funtional groups which show selective affinities for certain metals. "Chelating resins" have been produced with 8-hydroxyquinoline, which complexes with up

to 60 ions, iminodiacetic acid (for example, CHELEX-100), vinylacetylacetone etc. (Fifield and Kealey, 1983).

Ion-exchange resins can also be used for the non-selective preconcentration of analytes in water samples. By using a "mixed bed" of cation and anion exchange resins, electrolytes can be removed from a water sample and very pure water obtained. By treating the resin with acid, the analytes are transferred to a smaller volume, thus preconcentrating each element equally. As a non-selective technique it has the advantages and disadvantages of evaporation (4.3.2.5), with the exception of the retention of volatile phases which would be lost during evaporation. However there is a greater risk of contamination from the resin; Thompson and Walsh (1983) suggest that of the two techniques, evaporation is preferable.

Ion exchange resins are commonly used in the selective preconcentration of water samples. Koide *et al.* (1984) employed a single anion exchange bead to concentrate and separate cyanide, thiocyanide and/or chloride-complexed trace metals (gold, palladium and cadmium etc.) from sea-water. The sample, a resin bead, and a few glass beads to aid mixing were contained in a micro-pipette tip and rotated over night. The bead was subsequently analysed by AAS using a carbon-cup atomiser. By passing the solution through an anion exchange column prior to adsorption on the single bead concentration factors of 1000 were achieved.

De Baar and Brewer (1983) used CHELEX-100 to concentrate rare earth elements (REEs) and remove major ions from seawater samples prior to analysis by INAA. Sturgeon *et al.* (1980) preconcentrated seawater 25-fold with CHELEX-100 and successfully determined iron, copper, zinc and nickel by ICP-OES. The technique was not sensitive enough for the determination of cadmium, lead, cobalt and chromium

however, and was time-consuming due to the slow flow rates and time required to remove calcium and magnesium ions from the resin. Higher preconcentration factors were achieved using 8-hydroxyquinoline; seawater samples were concentrated 50 and 90 times by immobilising 8-hydroxyquinoline onto silica gel (Sturgeon *et al.*, 1981 and 1982). Reliable detection of lead, cobalt and chromium was still not possible, but the procedure was faster than the CHELEX method; reagents could be more easily purified and reused and it showed potential as a field-preconcentration technique. Watanebe *et al.* (1981) achieved a concentration factor of 200 prior to analysis by ICP-OES and claimed the technique's superiority over APDC-MIBK (4.3.2.2.) solvent extraction and CHELEX-100. This method has also been applied to analysis by ICP-MS (McLaren *et al.*, 1985).

Willie *et al.* (1983) immobilised 8-hydroxyquinoline on several resins and obtained optimal results when using a PVP (polyvinyl pyrrilodine) resin, XE305. Using this combination the iron level in the blank was significantly lowered and the problem of "chelate bleeding" due to hydrolysis, which typified earlier methods, did not occur.

Numerous investigations have been carried out into the optimal combination of chelating functional group and ion-exchange resin or alternative substrate, for the concentration of trace metals in water samples. However, in most cases analysis has been carried out by AAS, being more sensitive for some of the trace metals and more widely available. These studies include Samara and Kouimtzis (1985) who supported a new hydrazone on silica-gel, for the preconcentration of copper, zinc, lead, nickel, cobalt and cadmium; Stella *et al.* (1985) adsorbed cobalt on nitroso-R salt form DOWEX 1X8 and recovered it by elution with strongly acid titanium (III) chloride; Isshiki and Nakayama (1987) tested 14 different

ligands and two macroporous XAD resins, and identified the best combination for cobalt preconcentration of seawater samples; King and Fritz (1985) successfully preconcentrated cadmium, cobalt, copper, iron, mercury, nickel, lead and zinc by complexation with a dithiocarbamate followed by adsorption on XAD-4 resin and elution with methanol.

4.3.2.2 Solvent extraction

One of the most popular solvent extraction preconcentration methods involves the extraction of metal ions with pyrrolidine-N-carbodithioate into methyl isobutyl ketone, (Watanabe *et al.*, 1981). This technique has been widely used prior to determination by AAS and ASV (Brügmann *et al.*, 1983); however, the concentration factors are not generally great enough for determination by ICP-OES.

McLeod *et al.* (1981) achieved concentration factors of 250 - 500 times by the addition of a mixed complexing agent APDC and DDDC (ammonium tetramethylenedithiocarbamate and diethyl ammonium -diethyldithiocarbamate), buffering the solution at pH 4 and extracting the solution into chloroform. The detection limits were found to be suitable for the simultaneous determination of cadmium, copper, iron, molybdenum, nickel, vanadium and zinc by ICP-OES but not for lead, cobalt, chromium and manganese.

An example of single-element determination by ICP-OES following solvent extraction is described by Miyazaki *et al.* (1981). Reduced molybdoantimonylphosphoric acid was successfully extracted into DIBK and phosphorus in the extract determined down to 0.37 µg l^{-1} P. Only arsenic was found to interfere significantly.

4.3.2.3. Coprecipitation

Hiraide *et al.* (1976) described a simple preconcentration technique whereby heavy trace metals were coprecipitated with aluminium hydroxide, by adjusting the pH with ammonia or sodium

hydroxide, and bringing the precipitate to the solution surface with nitrogen bubbles; however, problems were encountered with excess magnesium and poor cadmium recoveries. By using indium hydroxide a concentration factor of 240 was obtained, facilitating the determination of cadmium, cobalt, chromium, copper, manganese, nickel and lead in natural waters by ICP-OES. The technique was claimed to be rapid and simple enough for use at the site of sampling (Hiraide *et al.* 1980)

Other hydroxides used to coprecipitate trace metals include lanthanum (Thompson *et al.*, 1981b) to coprecipitate arsenic, bismuth, antimony, selenium and titanium prior to ICP-OES by hydride generation, and ferric hydroxide (Wiesel *et al.*, 1984) to coprecipitate aluminium, lead and vanadium from seawater prior to determination by INAA and AAS. Ferric hydroxide has also been used to coprecipitate REEs in seawater (Martin *et al.*, 1976 and Elderfield and Greaves, 1982).

4.3.2.4 Electrochemical methods

An electrochemical technique for the preconcentration of trace metals for determination by ICP-OES was described by Long and Snook (1983). Within an electrochemical cell of wall-jet design, a glassy carbon electrode is held at the reduction potential of the metal of interest. The sample solution is pumped into the cell and the metal gradually deposits on the electrode, the accumulation being sufficient for determination after ten minutes. By applying an anodic-stripping potential the metal is rapidly stripped back into the electrolyte solution, which is then pumped to the nebuliser for measurement by ICP-OES. As with other selective techniques, trace elements are efficiently removed from solutions of high TDS content and can be introduced to the ICP in a matrix-free

solution thus avoiding nebuliser blockage and the production of stray light interferences.

4.3.2.5 Evaporation

The simplest method of raising the concentration of dissolved constituents in a water sample is by reducing the volume of solution by evaporation. As the method is non-selective it is not suitable for the preconcentration of high TDS samples as salt tolerances of standard ICP nebulisers are exceeded. In addition, high concentrations of calcium and magnesium cause matrix and spectral interferences and stray light problems in the spectrometer. However, because the technique is non-selective it is ideal for the preconcentration of fresh water samples, allowing, in theory, major and trace element determinations to be performed on one sample.

Thompson (1982a) described a batch-method for the 10-20 fold preconcentration of small volume samples prior to analysis by ICP-OES. The solutions are heated in test tubes retained in an aluminium block, with a precise amount of lanthanum added to each sample to allow for any variation in final volumes.

At Wallingford, water samples are routinely preconcentrated 20-times by evaporation under clean-room conditions (3.4). The final volume of 20 ml is sufficient for both simultaneous quantitative trace element analysis and a qualitative wavelength scan (3.2.4). This allows the spectral environment of each analyte to be checked, enabling background shifts etc. to be identified, and therefore more accurate results to be achieved.

4.3.2.6 Summary

Selective preconcentration techniques have achieved large concentration factors facilitating the determination of ultra-trace elements in seawater by AAS (particularly ETV-AAS), INAA etc. Greater concentration factors are required for ICP-OES, being a less

sensitive technique; however, even with 200 times (Watanebe *et al.*, 1981) and 250-500 times (McLeod *et al.*, 1981) preconcentration factors, there are still problems with certain metals - lead, cobalt, chromium and manganese. Unfortunately, contamination and blank levels increase with sample volumes, limiting practical concentration factors to 1000 (Thompson and Walsh, 1983), hence restricting the potential sensitivity of the technique.

4.3.3. Preconcentration of Lincolnshire Limestone groundwaters

The complete evaporation of water samples to solid residues with subsequent dissolution (3.3) and analysis by the Philips ICP-OES instrument, was selected as a method of preconcentration for Lincolnshire Limestone groundwaters for several reasons:

1. The experiment provided a unique opportunity to compare duplicate analyses of samples, presented to two ICP systems, in the state for which the instruments were set up for routine measurement; i.e. dissolved solid material by the Philips PV8490, dilute waters by the ARL 34000C.
2. Total evaporation was chosen since selective preconcentration methods would have removed minor cations (lithium, barium, strontium etc.) that were of interest as well as the trace metals. In addition, had the sodium chloride matrix been removed prior to evaporation by a selective method, there would not have been sufficient material to dissolve and analyse.
3. The method enabled further selective preconcentration procedures to be carried out on the residues, facilitating the determination of rare earth elements in the groundwaters.

4.3.3.1 Method

Five litre groundwater samples from the Lincolnshire Limestone aquifer were collected as described in 2.3. The weighed samples were evaporated to dryness under "clean room conditions"

(3.4) and the residues, varying in weight from 5 to 23 g, were oven-dried at 110°C for 70 minutes. The samples were prepared for major, trace and rare earth element analysis using the standard rock dissolution methods of fusion and acid-digestion (3.3) and subsequently analysed by ICP-OES (Philips) and flame AAS (3.3 and 4.4).

The concentration factor for each sample was calculated using the following formula (allowing for the conversion of ppm to mg l^{-1}):

$(M_a \times V_t)/(M_t \times \text{density} \times DF)$

Where: M_t = total weight of residue (g)

M_a = weight of residue used for analysis (g)

V_t = total volume of water evaporated (ml)

DF = dilution factor and Density = $1 - (TDS \times 10^{-6})$

Major elements (silicon, aluminium, iron, manganese, titanium, magnesium, calcium, sodium and potassium) reported as oxides and expressed on a weight percent basis in the residue analysis, were converted to elemental concentrations in the water. The lowest quantitatively determinable concentrations quoted for each element are presented in table 3.5A, however for most trace elements this was 2 mg kg^{-1} and for most major elements 0.02% oxide in the residue. Where a determination was below this level in the residue, the equivalent concentration in the water sample is indicated in the tables by a "less than" symbol (<). The same figures represent the error calculated for each analyte and are indicated by a plus-minus ($\pm$) symbol.

4.3.3.2 Results

Analyses of groundwater samples collected in both March (set A) and December 1985 (set B), using the "residue" technique are presented in Appendix 2. The ARL direct determinations on the groundwaters, ion balances for both the analyses and details of the

Table 4.2

CORRELATION COEFFICIENTS FOR MAJOR ELEMENTS DETERMINED IN GROUNDWATERS BY ICP-OES FOLLOWING DIFFERENT PRECONCENTRATION METHODS.

Groundwater samples were analysed directly by the ARL instrument; evaporation residues were determined by the Philips system. The two sets of samples were collected, treated and analysed at different times.

	Set A	Set B
Na	0.986	0.989
K	0.991	0.987
Ca	0.972	0.989
Mg	0.987	0.991
Sr	0.994	0.987
Ba	0.988	0.690
Li	0.994	0.989
SO_4	0.988	0.963
	(March 1985)	(Dec. 1985)

summarised.

The method enabled the waters to be concentrated up to 20 times for trace element analysis and 800 times for REE analysis, the concentration factors decreasing as the total mineralisation of each sample increased. Quotable concentrations of less than 1 $\mu g\ l^{-1}$ were obtained in some water samples.

The major and minor elements demonstrate good agreement although potassium values are consistently low and lithium and barium high. Correlation coefficients (table 4.3) indicate that sodium, potassium, calcium and magnesium concentrations for set B samples correlate more strongly with the ARL analyses than set A, however, even using these values with chloride and bicarbonate data (3.5) ion balances for the ARL analyses could not be improved (table 2.1A).

As set A samples were evaporated in a geochemistry laboratory and set B under "clean room" conditions, contamination of the former samples was anticipated, however, this has not occurred to a great extent. Although lithium values correlate well with the ARL direct measurements, set B results are consistently higher; similarly barium shows a relatively poor correlation coefficient (0.7) for set B. Chromium values are anomalously high in every sample. Contamination from sample preparation equipment during dissolution of the residues is suspected for chromium and barium, the PTFE crucibles used during acid-digestion being a known source of barium contamination; while $LiBO_2$ powder used as a flux (3.3) is a probable cause of the high lithium values.

The Lowest Quantitatively Determinable Concentrations for the residue method are not as low as those obtained routinely by the ARL instrument, with the exception of water samples in set A, which were analysed directly rather than after a twenty-times

preconcentration. Therefore "less-than" values for the trace elements cannot be improved upon. Concentrations of manganese and titanium were consistently below 0.02% oxide in the residue and most of the trace elements less than 2 mg kg^{-1}. Several samples did produce positive results however, (Quadring High Fen (set B), Cheal Bridge (A and B) and Sixscore Farm (A)), demonstrating contamination with cobalt, copper, zinc and aluminium in particular.

The REEs (table 2.2A) are present at very low concentrations in the aquifer, frequently <100 ng l^{-1}, and therefore only a few residues returned concentrations above chondritic abundance (selected as the LQDC for most elements). With such high concentration factors analyte levels in the blank can limit the sensitivity of the technique and unfortunately precluded the determination of REEs in samples from set A. However, it was possible to produce shale-normalised plots for five groundwaters and these are presented and discussed in chapter 6.

4.3.3.3 Discussion

The residues absorbed variable quantities of water during storage, and were therefore oven-dried at 110°C prior to preparation. The average weight loss was approximately 1%; however, as hydrated materials, they also contained water of crystallisation. A single sample (Bicker) was gradually heated and reweighed after drying at a constant temperature for 60 minutes. The cumulative weight loss was 1.7% at 200°C, 28.9% by 390°C and 29.7% by 700°C. At 900°C the residue fused to the porcelain crucible thus precluding the measurement of "Loss On Ignition". Five other samples heated to 400°C exhibited reductions in weight of 5-20%. Weight losses of this magnitude would have little noticeable effect on the subsequent analyses however, as the equivalent concentrations of error in the waters would be less than the analytical precision and therefore

Table 4.3 ANALYSIS OF GROUNDWATER FROM BICKER BOREHOLE:

Three sub-samples of the residue were oven-dried at different temperatures prior to dissolution, analysis and conversion of data to concentrations in the groundwater.

Temp.	110°C	390°C	700°C
	mg l^{-1}	mg l^{-1}	mg l^{-1}
Na	1279 ±1	n.d	n.d
K	5.3 ±0.3	5.4 ±0.3	5.2 ±0.3
Ca	18.7 ±0.6	19.0 ±0.6	19.0 ±0.6
Mg	12.0 ±0.5	13.0 ±0.5	12.2 ±0.5
Sr	1.9 ±0.1	1.8 ±0.1	1.8 ±0.1
	µg l^{-1}	µg l^{-1}	µg l^{-1}
Fe	555 ±277	549 ±275	684 ±273
Mn	<635	<612	<610
Ti	<1181	<1138	<1134
Al	<210	<208	<207
	±7.9	±7.9	±7.8
Ba	35.7	31.4	35.2
Co	<7.9	<7.9	<7.8
La	<7.9	<7.9	<7.8
Li	83.3	78.5	86.0
Nb	<7.9	<7.9	<7.8
Ni	<7.9	<7.9	<7.8
Sc	<7.9	<7.9	<7.8
V	<7.9	<7.9	<7.8
Y	<7.9	<7.9	<7.8
Zr	<7.9	<7.9	<7.8
	±19.8	±19.8	±19.6
Cr	59.5	47.1	46.9
Cu	<19.8	<19.8	<19.6
Zn	55.5	82.4	<19.6
	± 35.6	± 35.6	± 35.3
Ce	<35.6	<35.6	<35.3
Mo	<35.6	35.6	<35.3

within the reported concentration range. The exception would be strontium, present at much higher concentrations, hence this element is only quoted to 0.1 mg l^{-1} in the waters. To test these assumptions three sub-samples were dried at 110, 390 and 700°C and analysed. The data presented in table 4.3 demonstrate that any differences between the analyses are indeed less than the error calculated for each element. The choice of drying temperature (110°C) is therefore valid even if the water of crystallisation was not totally removed prior to analysis.

It had been hoped that lower detection limits than those of the ARL system would have been obtained, facilitating the quantification of some trace elements in the Lincolnshire Limestone. This was only possible for a few REEs which had not been determined previously, following an additional selective preconcentration method. However, in comparison with groundwaters from other U.K. aquifers, the water samples from the Lincolnshire Limestone contain very low levels of minor and trace elements. Groundwaters from the Sherwood Sandstone (Trias) for example, have generally higher concentrations of barium, lithium and manganese than the less-saline Lincolnshire samples, and more frequently exhibit concentrations of copper, zinc, nickel, cadmium, lead and arsenic that are above 0.1-1 µg l^{-1} (Edmunds *et al.*, 1982). Similarly, the concentrations of nickel, lead, zinc and chromium are higher in the groundwaters from the Carboniferous Limestone in Derbyshire (Edmunds, 1971) and oolitic limestones of Gloucestershire (Morgan-Jones and Eggboro, 1981) than in those derived from the Lincolnshire Limestone. As the trace analytes occur at such low levels, even with the concentration factors obtained, most could not be quantified and lower LQDCs than those acheived by the ARL instrument could not be attained.

4.3.4 Summary

Preconcentration methods for the determination of trace elements in water samples have been reviewed. Duplicate water samples were preconcentrated in different ways and presented to two ICP-OES systems in the form for which the instruments are currently set up for routine analysis. By evaporating groundwaters to a residue, subsequently dissolving the samples by standard rock-dissolution techniques and analysing them on the Philips PV4890, concentration factors of up to 20 and 800 were achieved for trace element and REE determinations respectively. Major and minor elements determined on the two systems demonstrate very strong positive correlations; however, lithium and barium contamination was a problem in the residues, and heavy metal contamination also occurred in a few samples. Trace elements present at the $\mu g\ l^{-1}$ level were below the LQDC for most elements, and therefore the "less than" values obtained by the ARL 34000C were not improved. New REE determinations on the waters were obtained however and these are discussed in 6.3.3.4.

4.4 SULPHUR DETERMINATIONS ON LIMESTONE GROUNDWATER RESIDUES USING THE PHILIPS PV4890 ICP SOURCE AND SOPRA SCANNING MONOCHROMATOR

4.4.1 Introduction

Total sulphur is routinely determined in groundwater samples on the ARL instrument using the most sensitive sulphur line, which is in the vacuum ultraviolet (180.73 nm). In the Lincolnshire Limestone groundwaters sulphur occurs mainly in the oxidised form, sulphate being present as a major ion (0.5-140 $mg\ l^{-1}$). Dissolved, reduced sulphur has also been detected in these groundwaters (4.2), although only at trace levels, the maximum concentration determined was 140 $\mu g\ l^{-1}$.

In rock samples sulphur is present mainly as finely divided sulphides which are volatilised as H_2S during sample preparation techniques involving $HF/HClO_4$ acid-digestions. Sulphur is therefore not normally determined during routine geochemical analysis. However, it was possible to determine sulphur in the $HF/HClO_4$ digestions of the groundwater residues as sulphur in these samples is present as sulphate-sulphur, which would be unlikely to be volatilised as sulphur dioxide during the sample preparation. Solutions were prepared from the residues by the $HF/HClO_4$ digestion method described in 3.3.2. The samples were analysed for trace elements (4.3) then for sulphur using the Philips ICP.

4.4.2 Method

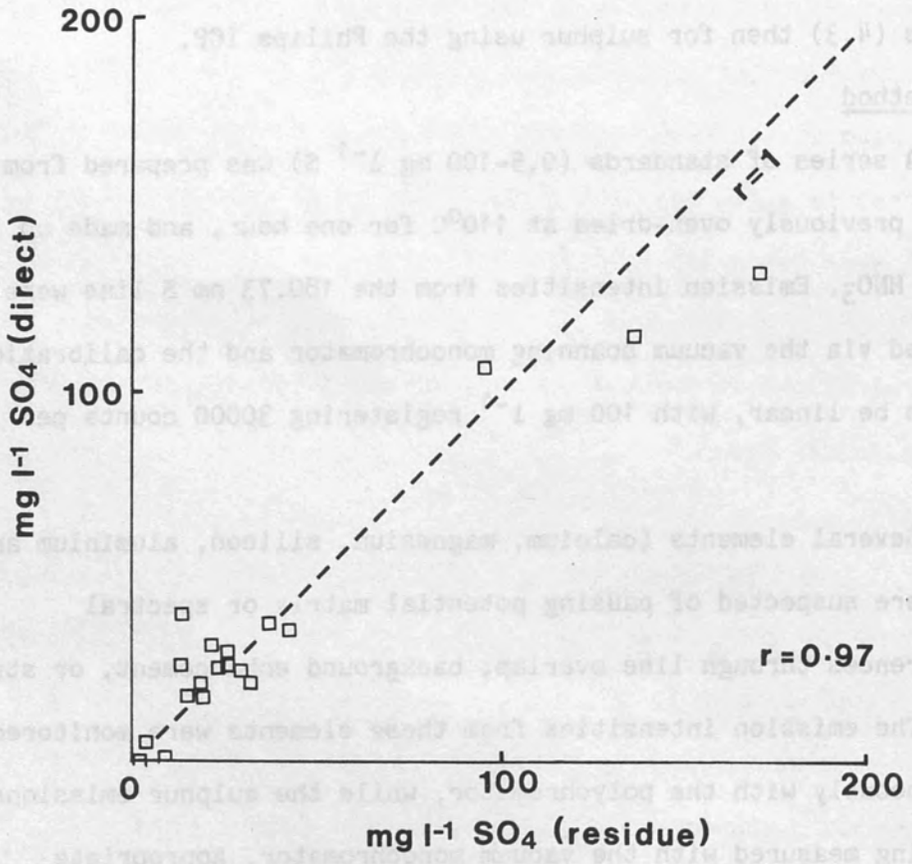
A series of standards (0.5-100 mg l^{-1} S) was prepared from Na_2SO_4, previously oven-dried at 110°C for one hour, and made up in 10% v/v HNO_3. Emission intensities from the 180.73 nm S line were monitored via the vacuum scanning monochromator and the calibration found to be linear, with 100 mg l^{-1} registering 30000 counts per second.

Several elements (calcium, magnesium, silicon, aluminium and iron) were suspected of causing potential matrix or spectral interferences through line overlap, background enhancement, or stray light. The emission intensities from these elements were monitored simultaneously with the polychromator, while the sulphur emissions were being measured with the vacuum monochromator. Appropriate corrections were necessary for calcium (line overlap) and for minor interferences from magnesium and silicon (background shift), however, the concentrations of iron and aluminium in most solutions was sufficiently low for corrections not be be required.

The corrected intensities were converted to sulphur concentrations and multiplied by the appropriate factor for each

Figure 4.6

Correlation of sulphate determinations in groundwater samples by two ICP-OES systems. Direct determinations were performed by the ARL instrument, evaporation residues were determined by the Philips system.



residue sample, to give sulphate concentrations for the original water samples, in mg l^{-1}.

4.4.3 Results

The sulphate determinations on the residues compare reasonably well with direct measurements carried out by the ARL system (table 2.1A; figure 4.6). No bias in the two sets of results was identified and the correlation coefficient for the 19 samples, ranging from 0-150 mg l^{-1} SO_4, was 0.97.

The lack of a consistently lower set of results for the residues and their good correlation with the direct sulphate determinations, indicate that sulphur was not lost to a significant extent during sample preparation.

The precision, detection limit and background equivalent concentration of the technique were evaluated. The routine precision of the method is fair; a mean relative standard deviation of 2.7% was obtained from measurements of the concentration of several standards, repeated at regular intervals during the four-hour period of analysis.

The 3σ detection limit calculated from eleven consecutive blank (10% HNO_3) measurements was 0.33 mg l^{-1} SO_4; the background equivalent concentration was 4.38 mg l^{-1}. However, the total dissolved solid content of each groundwater sample varied widely. The 3σ detection limits for the Lincolnshire Limestone groundwater samples therefore ranged from 0.016-0.19 mg l^{-1} SO_4, for samples with the lowest and highest TDS.

4.5 WATER ANALYSIS ON THE PHILIPS ICP SYSTEM

4.5.1 Introduction

The Philips ICP instrument is routinely used for the determination of major, trace and rare earth elements in rock and soil samples. An analytical program, "WATERS", was also set up on the Philips system, to facilitate the determination of seven major ions in natural waters.

4.5.2 Standards

Stock standard solutions were prepared from Specpure salts (Na_2CO_3, $CaCO_3$, K_2CO_3, $SrCO_3$ and MgO) and atomic absorption standard solutions (1000 mg l^{-1} Li and B). The carbonates were first dried at 120°C for 70 minutes; the MgO at 480°C for the same period. Multielement calibration standards were prepared by serial dilution of the stock solutions in the following ranges: 1-2500 mg l^{-1} Na; 1-100 mg l^{-1} Ca; 1-20 mg l^{-1} K, Mg and Sr; 0.1 mg l^{-1} B and 0.01-1 mg l^{-1} Li. The standards were acidified to 1% v/v HCl to match the groundwater samples collected from the Lincolnshire Limestone aquifer.

4.5.3 Software

Appropriate software lists were set up to enable calibrations to be prepared and stored, analyses to be performed and daily restandardization to be undertaken.

4.5.4 Operating conditions

Operating conditions used during the analysis of trace element solutions of rock samples (3.3) were found to be satisfactory for the "WATERS" program. The power settings and argon

flow rates are presented in table 3.3. However, the high voltage settings for each photomultiplier tube had to be reduced considerably. Emission intensities on the sodium 588.99 nm line were too high even on the minimum HV setting, and the insertion of a capacitor was necessary to prevent the measured intensities exceeding 30000 counts per second.

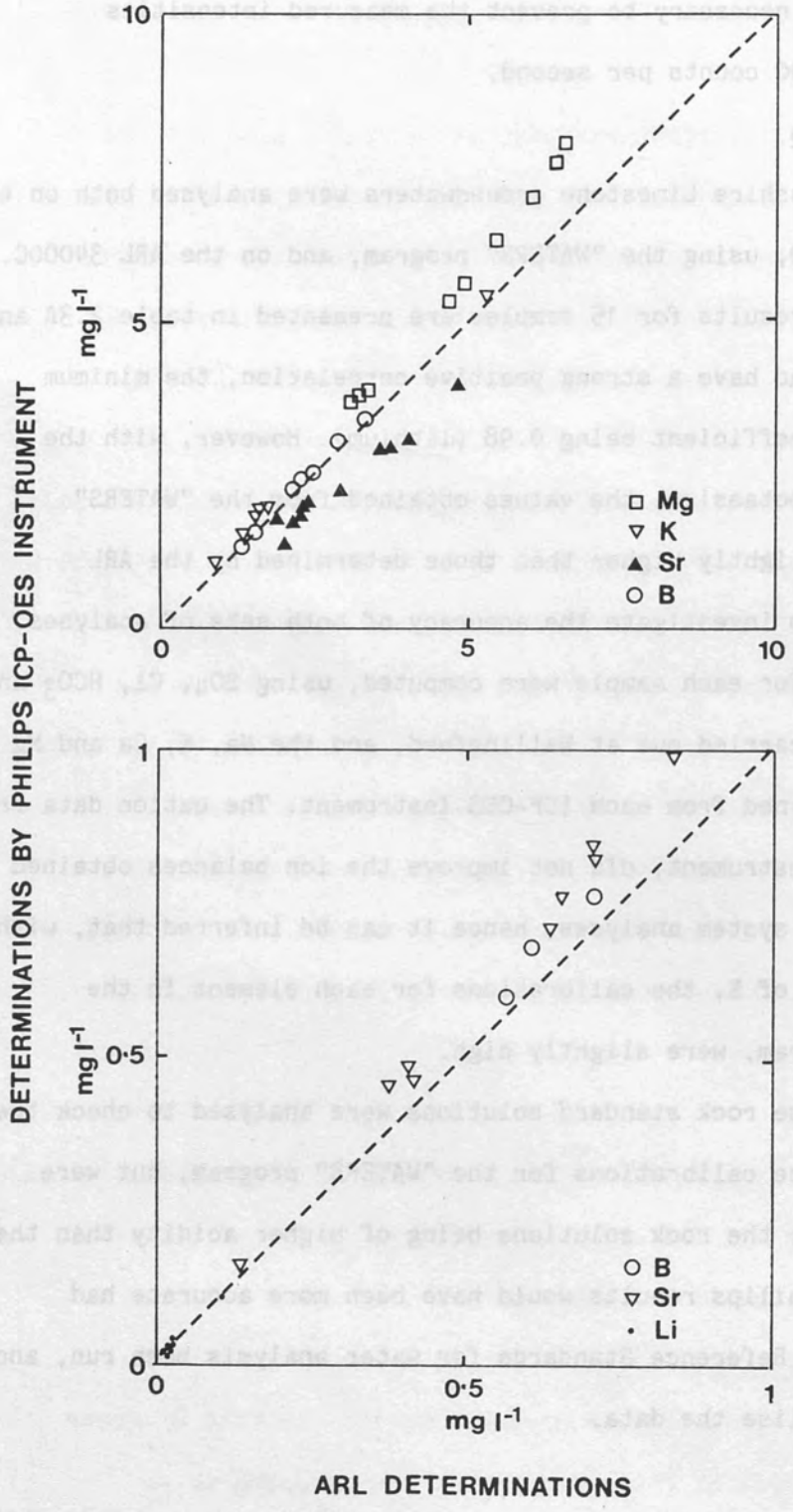
4.5.5 Analysis

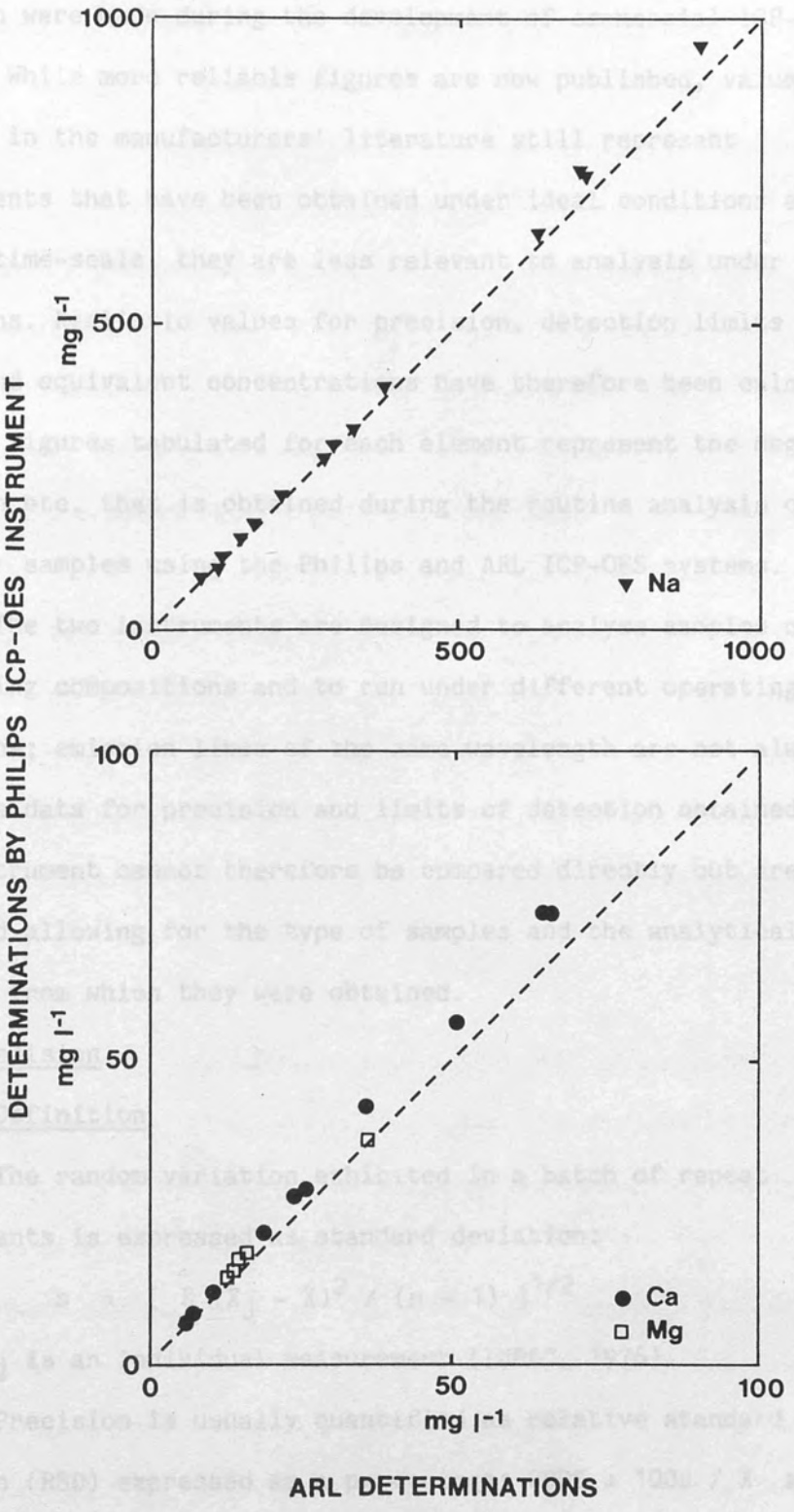
Lincolnshire Limestone groundwaters were analysed both on the Philips PV8490, using the "WATERS" program, and on the ARL 34000C. Both sets of results for 15 samples are presented in table 2.3A and figure 4.7, and have a strong positive correlation, the minimum correlation coefficient being 0.98 (potassium). However, with the exception of potassium, the values obtained from the "WATERS" program are slightly higher than those determined by the ARL instrument. To investigate the accuracy of both sets of analyses, ion balances for each sample were computed, using SO_4, Cl, HCO_3 and NO_3 analyses carried out at Wallingford, and the Na, K, Ca and Mg analyses obtained from each ICP-OES instrument. The cation data from the Philips instrument, did not improve the ion balances obtained using the ARL system analyses, hence it can be inferred that, with the exception of K, the calibrations for each element in the "WATERS" program, were slightly high.

In-house rock standard solutions were analysed to check the accuracy of the calibrations for the "WATERS" program, but were inappropriate; the rock solutions being of higher acidity than the waters. The Philips results would have been more accurate had International Reference Standards for water analysis been run, and used to normalise the data.

Figure 4.7

Correlation of direct determinations of major ions in groundwater samples by the ARL and Philips ICP-OES systems.




1000
500
0
mg l-1
0
500
1000
▼ Na
100
50
0
mg l-1
0
50
100
mg l-1
● Ca
□ Mg
DETERMINATIONS BY PHILIPS ICP-OES INSTRUMENT
ARL DETERMINATIONS

4.6 PRECISION AND DETECTION LIMITS FOR ROUTINE ANALYSIS BY ICP-OES

4.6.1 Introduction

Claims for outstanding detection limits and excellent precision were made during the development of commercial ICP-OES systems. While more reliable figures are now published, values reported in the manufacturers' literature still represent measurements that have been obtained under ideal conditions and over a short time-scale, they are less relevant to analysis under routine conditions. Realistic values for precision, detection limits and background equivalent concentrations have therefore been calculated. The mean figures tabulated for each element represent the degree of precision etc. that is obtained during the routine analysis of rock and water samples using the Philips and ARL ICP-OES systems.

The two instruments are designed to analyse samples of contrasting compositions and to run under different operating conditions; emission lines of the same wavelength are not always used. The data for precision and limits of detection obtained for each instrument cannot therefore be compared directly but are discussed allowing for the type of samples and the analytical programs from which they were obtained.

4.6.2 Precision

4.6.2.1 Definition

The random variation exhibited in a batch of repeat measurements is expressed as standard deviation:

$$s = \left[\sum_{j=1}^{n} (X_j - X)^2 / (n - 1) \right]^{1/2}$$

where X_j is an individual measurement (IUPAC, 1976).

Precision is usually quantified as relative standard deviation (RSD) expressed as a percentage: RSD% = 100s / X as recommended by IUPAC (1976). Unless otherwise stated, X refers to

concentration data not intensities throughout this section.

4.6.2.2 Method

Several hundred determinations were obtained on a variety of solutions using the major, trace and rare earth element programs on the Philips ICP. The solutions included igneous rock standards, synthetic standards, limestone solutions and groundwater residue solutions (4.3). Precision under short term conditions was evaluated by continuously nebulising a single sample throughout the measurements, ("contiguous integrations", Thompson and Ramsey, 1985). For the evaluation of medium term precision the measurements were carried out over several hours; the test solution was not nebulised continuously, but for long enough to achieve signal stabilisation and integration. Samples were alternated with blanks and with other samples of differing composition. Longer term precision, allowing for day-to-day variations was evaluated over nine months.

A variety of solutions were also used during the evaluation of precision on the ARL instrument - dilute groundwaters, spiked seawater dilutions, standards etc. The mean RSDs calculated for each element on both the ARL and Philips ICP systems are presented in appendix 3.

4.6.2.3 Results

On the Philips PV4890 three analytical programs are used for the routine determination of major, trace and rare earth elements in rock samples. The dissolution procedures and operating conditions for each program are described in 3.3.3.

Rock samples were initially diluted 500 times prior to analysis for major elements, however, to improve precision by reducing the concentration of lithium metaborate entering the ICP, this factor was increased to 2000 in summer 1986, and is therefore appropriate to the analysis of groundwater residues (4.3). For both

dilutions, 150 measurements were carried out and the results in table 3.1A demonstrate an improvement in instrumental precision for certain elements, notably Ca, K and Na, with the increased dilution factor. The overall RSDs for the method are 5.4% and 4.5% for the 500 and 2000-times dilutions respectively. However, the RSDs for Fe, Mg, P, Mn, Ni and Cr, deteriorate in the most dilute major element solution as they were present only as minor elements in the limestone and groundwater residue solutions. The solutions for trace element determinations were more appopriate for the determination of all elements (except Si, Ca and Na) in the Lincolnshire Limestone samples, as they involve only a 100-fold dilution of the rock sample; precision is markedly improved over the "major element solutions", with an overall RSD of only 2.7%. The overall dilution factor of samples for REE analysis is only 10. Precision was good, the mean RSD of all the elements being 2.3%

Precision measurements on the ARL system are generally considerably better than for the Philips with an overall mean of just 1.2%. As the trace elements in the Lincolnshire Limestone groundwaters were usually too low for the direct determination of these elements for precision measurements, groundwaters and seawater dilutions were spiked with trace metals to complete the calculation of the RSDs.

4.6.2.4 Discussion

There are many factors which may contribute to deterioration in instrumental precision to varying degrees. Fassel (1986) summarised the main causes of variation in precision as:

1. Flicker noise fluctuations
2. Temporal fluctuations and drift in:
   a. Sample solution uptake rate
   b. Aerosol carrier gas flow rate

c. Nebulisation efficiency

d. Aerosol transport and injection efficiency

e. Torch box air temperature

f. Warm-up drift

g. RF power delivered

h. Detector sensitivity

3. Differences in replicate analyte solution temperatures, acidities, viscosities or surface tensions.

Of the above variables, poor precision due to instrument warm-up drift is avoided during routine analysis by leaving a sufficient warm-up period prior to analysis. However, the influences of day-to-day instrumental drift and differences of sample matrices etc. were allowed for in the realistic precision figures; measurements were carried out at different times of the day, over nine months and on samples of varying composition. Analytical precision (which includes errors introduced during sample preparation) is also accounted for; a number of standard solutions of the same composition, but prepared at different times, were included in the calculations.

The mean RSDs give a good indication of the precision of the analyses presented in chapter 5. However, as the RSDs deteriorate as the detection limit is approached, and particularly low concentrations were omitted, the precision of determinations of very low abundances will tend to be worse than the tabulated figures.

In comparison with the levels of analytes determined in silicate rocks, the determinands in the rock and residue samples from the Lincolnshire Limestone are very low; the majority of determinations in these samples was thus carried out in the solutions prepared for trace element analysis. Line curvature and/or volatilisation precluded the determination of sodium (residues),

calcium (limestones) and silicon (both sample sets) in the "trace element solutions", therefore precision for these elements is relatively poor. Major element solutions were diluted 500 and 2000 times during the preparation of rock and groundwater residue samples respectively (3.3.1), the RSDs appropriate to these determinations are therefore 3.6% (Si), 5.3% (Na) and 1.9% (Ca) for the residues, and 3.8% (Si), 2.3% (Na) and 4.8% (Ca) for the rock samples.

Consistently superior precision measurements were obtained on the ARL than on the Philips ICP system. This is to be expected when the types of solutions analysed by each instrument are compared. Only dilute waters are analysed on the former, whereas solutions of varying acidities, dilution factors and concentration ranges are run on the Philips instrument. To avoid the problem of matrix interferences all samples and standards are matrix matched. However, for each type of solution, gas flow and power settings are manually altered, introducing the possibility of increased variation in these instrumental conditions and therefore in drift. In comparison, the operating conditions for the ARL are maintained unchanged, for months at a time.

4.6.2.5 Summary

The realistic precision figures presented in this section (2.3-5.4% RSD for rocks, 1.2% for waters) indicate that adequate instrumental precision is possible over several months, short-term precision usually being considerably better. However, alternative analytical methods used in geochemistry offer much lower RSDs, for example solids analysis by XRF, and it is expected that the precision of ICP-OES may improve in the future. The use of internal standards, although not without problems, has been useful in this area; Ramsey and Thompson (1985), for example, improved medium term precision with the use of the Parameter-Related Internal Standard Method (PRISM

model). It is thought that better control of nebulization variables, particularly injector gas flow rate, could be significant in improving instrumental precision (Thompson and Walsh, 1983).

4.6.3 Detection limits and background equivalent concentrations

4.6.3.1 Definitions

Three sigma (3σ) detection limits are defined as three times the standard deviation of n intensity measurements on a "blank" solution, multiplied by the slope of the calibration function to give the equivalent concentration. The background equivalent concentration (BEC) refers to the analyte concentration that produces an emission signal equal to the intensity of the plasma background at any selected wavelength.

Slope, detection limit and BEC are calculated thus:

$$\text{Slope, } M = (C_H - C_B) / (I_H - I_B)$$

$$3\sigma \text{ detection limit} = 3\sigma_{IB} \times M$$

$$\text{BEC} = I_B \times M$$

σ = standard deviation

Where:

C_B = concentration of "blank"

C_H = concentration of "high" standard

I_B = intensity of "blank"

I_H = intensity of "high" standard

The use of 3σ rather than 2σ detection limits is recommended by IUPAC (1976).

4.6.3.2 Method

Manufacturers' figures for detection limits are often achieved only under ideal conditions, over the shortest possible time scale and while a solution is being continuously nebulised. More realistic conditions were simulated for the determination of 3σ detection limits on both ICP systems. The standard deviation of

intensity measurements on replicate "blanks" was calculated from continuously nebulised blank solutions, blanks which were alternately nebulised with sample solutions and on blanks included at regular intervals during routine analysis. As with the measurement of precision, various samples and standards were used as the high concentration solutions for the calculation of the slope, in order to recreate typical conditions.

4.6.3.3 Results

Aqueous 3σ detection limits for both instruments are presented in table 3.3A. With the exception of Si, Ca and Zr, the detection limits are in the range 0.3-400 mg kg^{-1}. In comparison with the ARL instrument, values for the Philips system are slightly higher for Na, Li, Sr and V; an order of magnitude higher for Al, Ca, Mg, K, Cu, Sc, Zn and Zr; and significantly higher for Si, Fe and Mn. Detection limits for Ni, P, Ba and Co are lower on the Philips instrument and REE figures are all below 0.1 μg kg^{-1}.

The aqueous detection limits are achievable in waters, but detection limits for rock samples are degraded by factors of 10 for the REEs, 2000 for Si and Zr, and 100 for all other elements on the Philips instrument, as these are the factors by which the rocks are diluted during sample preparation. Detection limits and background equivalent concentrations obtained in the sample are presented in tables 3.4A and 3.2A respectively.

4.6.3.4 Discussion

The two sets of aqueous detection limits presented in table 3.3A, are within an order of magnitude of each other for most elements, with values generally lower for the ARL instrument. Silicon and zirconium cannot be reliably determined in samples prepared by acid-digestion, therefore the detection limits have been calculated from solutions prepared by fusion of the sample with $LiBO_2$ for the

determination of major elements in silicate rocks. The samples are diluted 2000 times to obtain reasonable precision, hence the poor detection limits for these elements in the rock sample (2.24 and 0.087 mg kg^{-1} for silicon and zircon respectively), although they are quite adequate for routine geochemical analysis.

The differences between detection limits obtained for each element, on both systems, partly reflect the concentrations at which they naturally occur. For example, Si, Al, Ca, Fe, Mg, Na and K are all major constituents of rock samples; the upper part of the calibration curve is of greatest interest for these elements and emission signals may be reduced by selecting less sensitive lines, or by turning down the HV settings on the photomultiplier tubes (3.3). Low detection limits for these elements on the Philips system are not therefore important. Even allowing for dilution during sample preparation, the limits of detection for these elements fall well below the equivalent of 0.01% (100 mg kg^{-1}) oxide to which they are normally reported. Similarly in water analysis it is less important to achieve very low detection limits for the major elements Na, K, Ca, Mg, S and Si. By comparision, detection limits for the trace element program are excellent, with values well below concentrations normally encountered in silicate rock samples. Trace elements are reported to the nearest mg kg^{-1}, which is higher than most of the detection limits calculated here. The figures indicate however, that Ce, Cr and Zn cannot be reported reliably below 3 mg kg^{-1} and Cu below 4 mg kg^{-1}.

Lower detection limits are required for the analysis of groundwater samples than rocks, since the former are dilute solutions with significantly lower abundances of most elements. However, the elements Co to Pb in table 3.4A and in particular Ni, Mo, Al and Pb are not as sensitive as would be desired. In many natural waters

these elements occur at concentrations below these instrumental limits of detection.

In practise, 3σ detection limits are not a realistic indication of those obtainable on a routine basis, even when carrying out the measurements under rigorous conditions, since they do not allow for minor interferences which raise practical limits of detection. For example, stray light interference from calcium at the concentrations typical of pure limestones (56% CaO), causes a response from Al and Ti equivalent to 0.02% Al_2O_3 (53 mg kg^{-1} Al) and 0.03% TiO_2 (120 mg kg^{-1} Ti) and therefore limits the determination of aluminium and titanium in Lincolnshire Limestone samples to these levels.

In water analysis, a "Lowest Quantitatively Determinable Concentration" (LQDC) is useful as a lower limit of determination under routine conditions, and on the ARL is set at five times the 3σ detection limit. If a measured concentration falls below the LQDC for that element during routine analysis, it is automatically indicated on the printout. This alerts the operator to the fact that further investigation (such as the analysis of a preconcentrated sample), will be necessary, if such low values are to be reported reliably. The LQDCs calculated for this investigation are presented in table 3.5A.

The LQDCs used for the analysis of rock and groundwater residues from the Lincolnshire Limestone on the Philips instrument are also presented in table 3.5A. For most of the major elements a figure of 0.02% oxide was appropriate, with the exceptions of SiO_2, TiO_2 and P_2O_5 while 2 mg kg^{-1} was suitable for the trace elements apart from Cr, Cu and Zn (5 mg kg^{-1}) and Ce and Mo (9 mg kg^{-1}). These are fairly conservative in comparison with detection limits obtained by Church (1981), but similar to the realistic limits reported by

Walsh and Howie (1986). In practise, the concentrations of REEs found in chondritic meteorites are realistic limits for quotable concentrations. Chondritic abundance is therefore used as the LQDC for most REEs although two times chondritic abundance is more appropriate for Ho, Er and Lu, 5 times for Gd and 15 times for Pr (table 3.5A).

4.6.4 Summary

Under routine conditions, average relative standard deviations of 2.3-5.4% in rocks and 1.2% in waters can be obtained. Although these figures are adequate for routine analysis and precision over shorter periods of time are better, improvements should be possible as developments in software and the sample introduction systems for ICP-OES progress.

Aqueous 3σ detection limits are within an order of magnitude for most elements on the two systems. While realistic detection limits in the sample are quite adequate for the determination of many elements in most groundwater samples and silicate rocks, this is not the case for the direct analysis of the purer limestone and groundwater samples from the Lincolnshire Limestone aquifer.

Preconcentration facilitates the determination of trace elements to much lower levels (4.3). The detection limits quoted in the analysis of the preconcentrated Lincolnshire limestone groundwaters were obtained by careful examination of the spectral scans, enabling the effects of background shift and spectral interference to be investigated more carefully. However, the trace elements Be, Cd, Co, Cr, La, Mo, Ni, Pb, Sc, V, Y and Zr were all present at concentrations below the detection limits even after preconcentration and cannot therefore be reported reliably.

4.7 SUMMARY

The principle analytical technique employed to investigate the hydrogeochemistry of the southern Lincolnshire Limestone was inductively coupled plasma-optical emission spectrometry. Two multielement simultaneous systems were used - a Philips PV4890 1.5 m airpath and a ARL 34000C 1 m vacuum instrument for the analysis of limestones and groundwaters respectively.

The hardware and operating conditions of the systems were compared in chapter 3; in this chapter detection limits and levels of precision obtainable under non-ideal conditions were evaluated. Relative standard deviations in the 1-5% and 0.5-2% ranges for the Philips and ARL instruments respectively, are adequate for routine rock and groundwater analysis. Aqueous 3σ detection limits for the two instruments are generally within an order of magnitude of each other, but realistic limits are degraded by dilution factors, interference effects etc. The LQDCs (lowest quantitatively determinable concentrations) selected for groundwater analysis are in the 0.1-100 $\mu g\ l^{-1}$ range, equivalent to five times the 3σ detection limit. For trace element determinations, however, wavelength scans were also employed to check the spectral background of each peak. On the Philips instrument, the detection limits selected were 2 $mg\ kg^{-1}$ for most trace metals with the exceptions of Cu and Zn (5 $mg\ kg^{-1}$) and Mo (9 $mg\ kg^{-1}$). Working detection limits for the determination of REEs in limestones and groundwater residues, were considerably higher than the 3σ detection limits; the value selected for the least sensitive line, praseodymium, was 1.8 $mg\ kg^{-1}$.

Novel sample pre-treatment techniques were devised to extend the range of determinations available for the analysis of Lincolnshire Limestone groundwaters, including the successful determination of dissolved sulphide down to the 1 $\mu g\ l^{-1}$ level using

a gas-liquid separator. The method was found to be more appropriate to the concentrations encountered in the limestone groundwaters than the ion selective electrode.

The total evaporation of five litre groundwater samples to a solid residue, with subsequent digestion by standard rock dissolution methods, facilitated the determination of rare earth elements in the groundwaters. Lanthanum is in the <0.1-1 $\mu g\ l^{-1}$ range, i.e. five or six orders of magnitude below that of a standard shale. Trace metal levels, including titanium and niobium, which were not determined on the ARL system were found to be below the limits of detection. However, correlation of the major and minor element data sets were excellent, with correlation coefficients greater than 0.97 for 8 elements, with the exception of barium (0.7) where contamination of one sample set during sample preparation was suspected. Sulphate was also determined in the residues, using the Philips ICP source in conjunction with the vacuum monochromator.

A program for water analysis was set up on the Philips instrument. Determinations of Na, K, Ca, Mg, B and Li using this programme, correlated well with duplicate determinations by the ARL water analysis programme; however, ion balances of the analyses demonstrated that the ARL determinations could not be improved upon.

CHAPTER FIVE

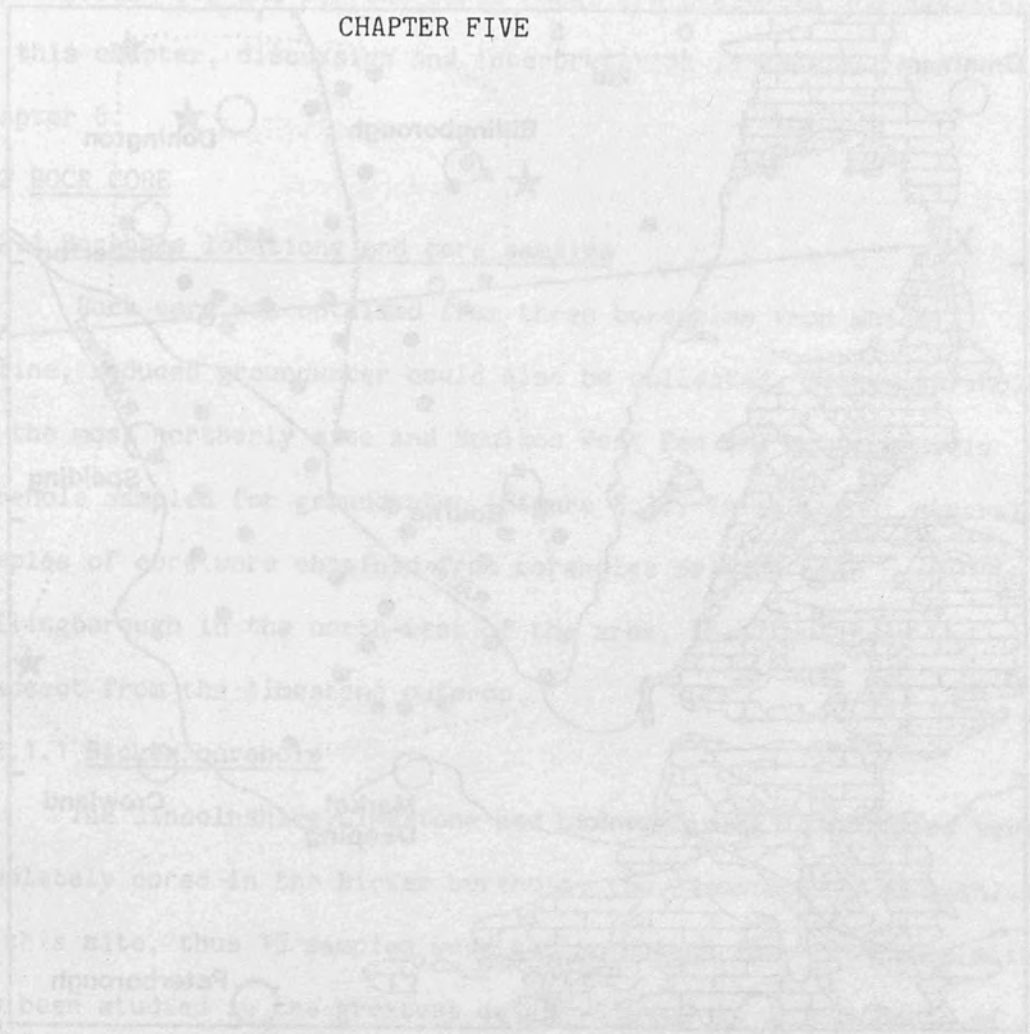
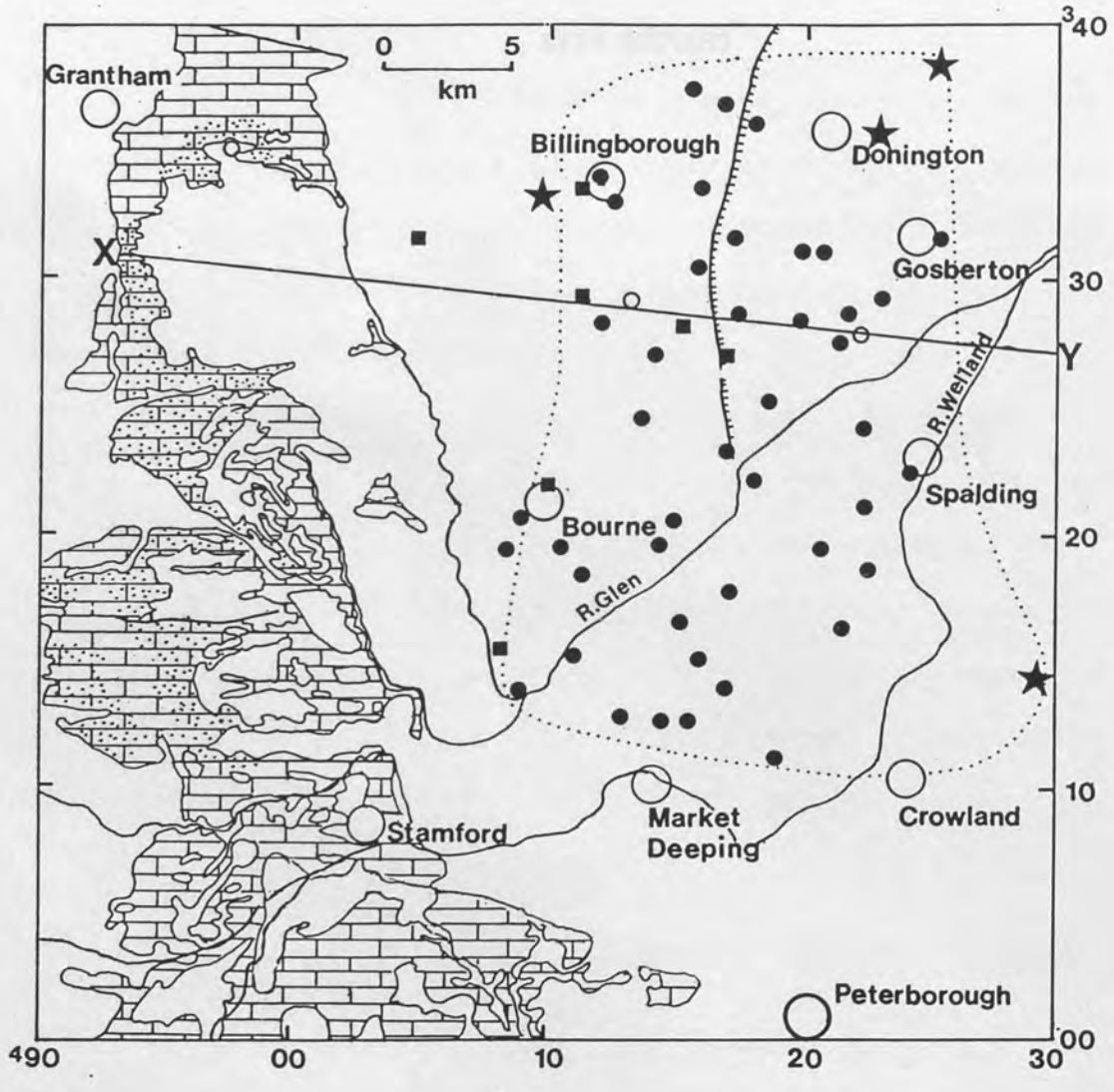


Figure 5.1

Map of the sampling area indicating borehole locations from which rock core (stars) and groundwater samples were obtained. Groundwaters collected under artesian flow in 1984/1985 are represented by solid circles; other samples collected by BGS in 1982/1983 are represented by open circles (artesian sites) and solid squares (public supply pumping stations). Line X-Y is the transect along which "distances from outcrop" (figure 5.8) were calculated. Other details of the legend are as in figure 1.2. (p. 21).



5: ANALYTICAL DATA FOR SAMPLES OF ROCK CORE AND GROUNDWATER FROM THE LINCOLNSHIRE LIMESTONE AQUIFER

5.1 INTRODUCTION

Groundwater and cored rock samples were collected from the Lincolnshire Limestone and subsequently analysed as outlined in chapters 2 to 4; the hydrogeology and hydrochemistry of the aquifer is reviewed in chapter 1. Data for the groundwater samples collected in December 1985 and for the cored rock, are presented and described in this chapter, discussion and interpretation is reserved for chapter 6.

5.2 ROCK CORE

5.2.1 Borehole locations and core samples

Rock core was obtained from three boreholes from which saline, reduced groundwater could also be collected. Bicker borehole is the most northerly site and Moulton West Fen the most easterly borehole sampled for groundwater (figure 5.1). In addition, several samples of core were obtained from boreholes drilled near Billingborough in the north-west of the area, 15-17 km along the transect from the limestone outcrop.

5.2.1.1 Bicker borehole

The Lincolnshire Limestone and its confining lithologies were completely cored in the Bicker borehole. The limestone is 35 m thick at this site, thus 15 samples were collected and core from this site has been studied in the greatest detail. Sample B1 from a depth of 97 m represents the Blisworth Limestone (formerly the Great Oolite) facilitating the comparison of the Lincolnshire Limestone with another oolitic aquifer; B2 and B3 (99.3 and 106.6 m below datum, respectively) represent the Upper Estuarine Series which confines the Lincolnshire Limestone from above, B2 being from a shell bed and

B3 a fine sandstone; B4-B15 (107.3, 110.0, 112.3, 113.1, 114.3, 118.1, 119.6, 125.4, 129, 130.5, 131.8 and 133.3 m) are from the aquifer itself. Sample B4 (Clipsham Member) is from just below the contact with the Upper Estuarine Series and B15 from just above the boundary with the underlying Grantham Formation (previously known as the Lower Estuarine Series).

The relative positions of the samples within Bicker borehole, are indicated in figure 5.2., the plot of analytical data versus depth of core in the borehole. The revised stratigraphy for the core after Ashton (1980) and Emery (*pers. comm.*, 1985) is also included.

5.2.1.2 Donington borehole

The borehole was drilled to a depth of 111.7 m below datum to prove the base of the Lincolnshire Limestone. Although the limestone is 25 m thick at this site, only the top 5 m of the aquifer was cored. Five samples were obtained from the Upper Lincolnshire Limestone, D1 (Clipsham Member) being from just below the contact with the overlying Upper Estuarine Series. The positions of the samples within the borehole and the revised stratigraphy for the available core (Emery, *op cit.*) are presented in figure 5.3.

5.2.1.3 Moulton West Fen Borehole

The Lincolnshire Limestone is only 12 m thick at this site, therefore just three samples (M2-M4) were taken of the aquifer at depths of 100, 102 and 109 m below datum. The lower part of the Upper Estuarine Series is represented by M1 (98.6 m). The positions of the samples relative to the whole of the cored section and the stratigraphy of the core are presented in figure 5.3.

5.2.1.4 Billingborough borehole

During a study into the extent of nitrate pollution in the Lincolnshire Limestone, BGS drilled several boreholes around

Figure 5.2

Major and trace element data for rock samples from Bicker borehole plotted against depth. Detection limit for each determinand indicated.

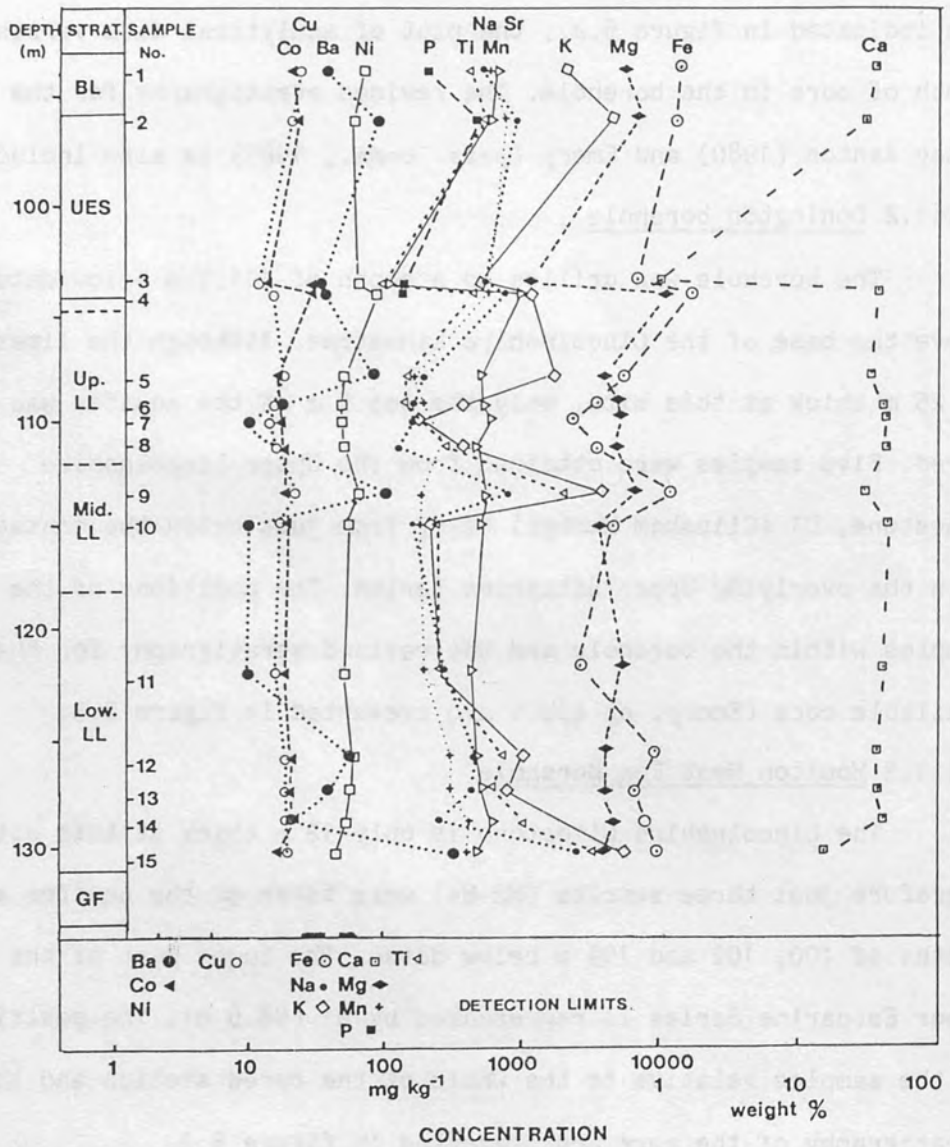


Figure 5.2 continued

BL = Blisworth Limestone, UES = Upper Estuarine Series, Up., Mid. and Low. LL = Upper, Middle and Lower Lincolnshire Limestone, GF = Grantham Formation.

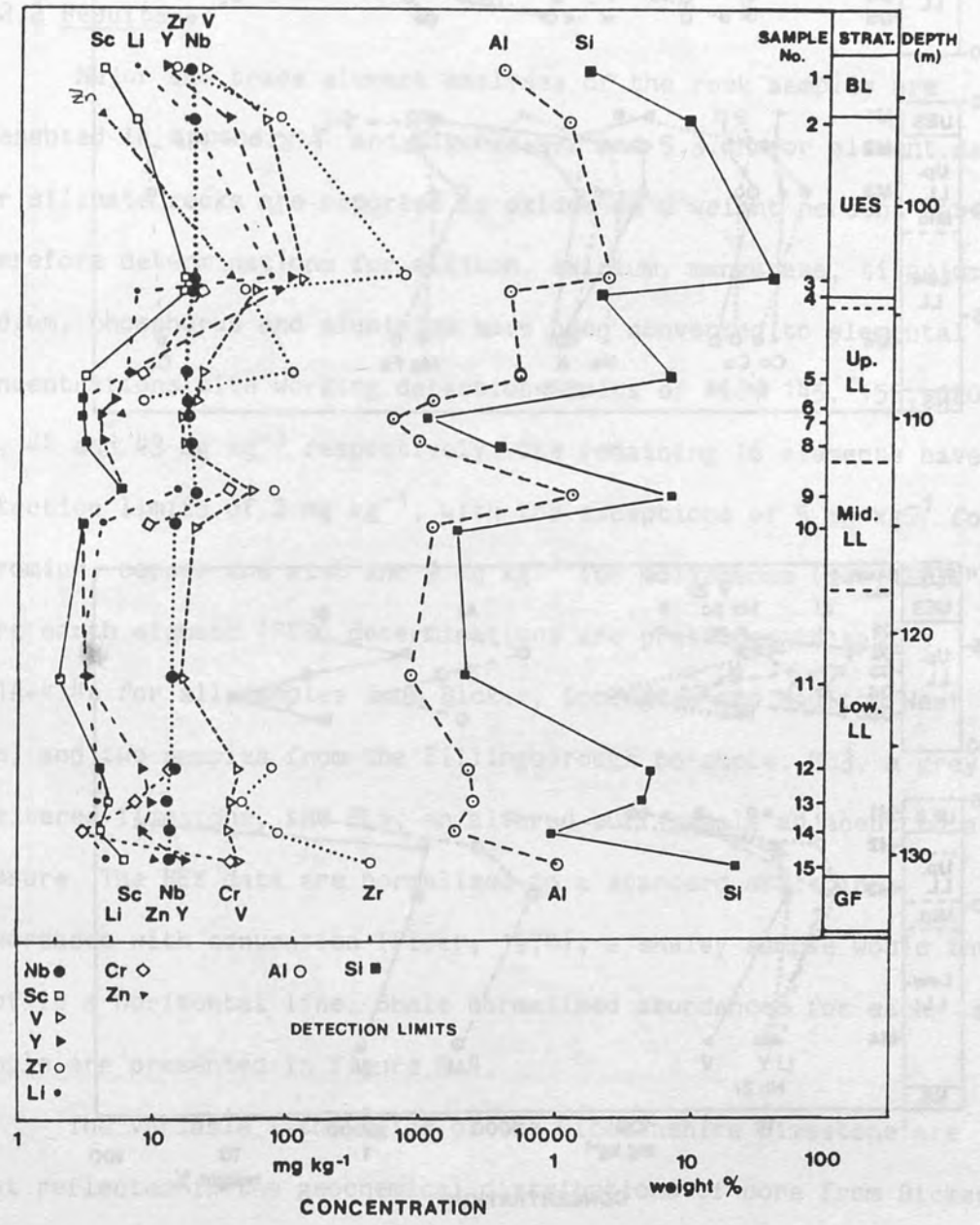
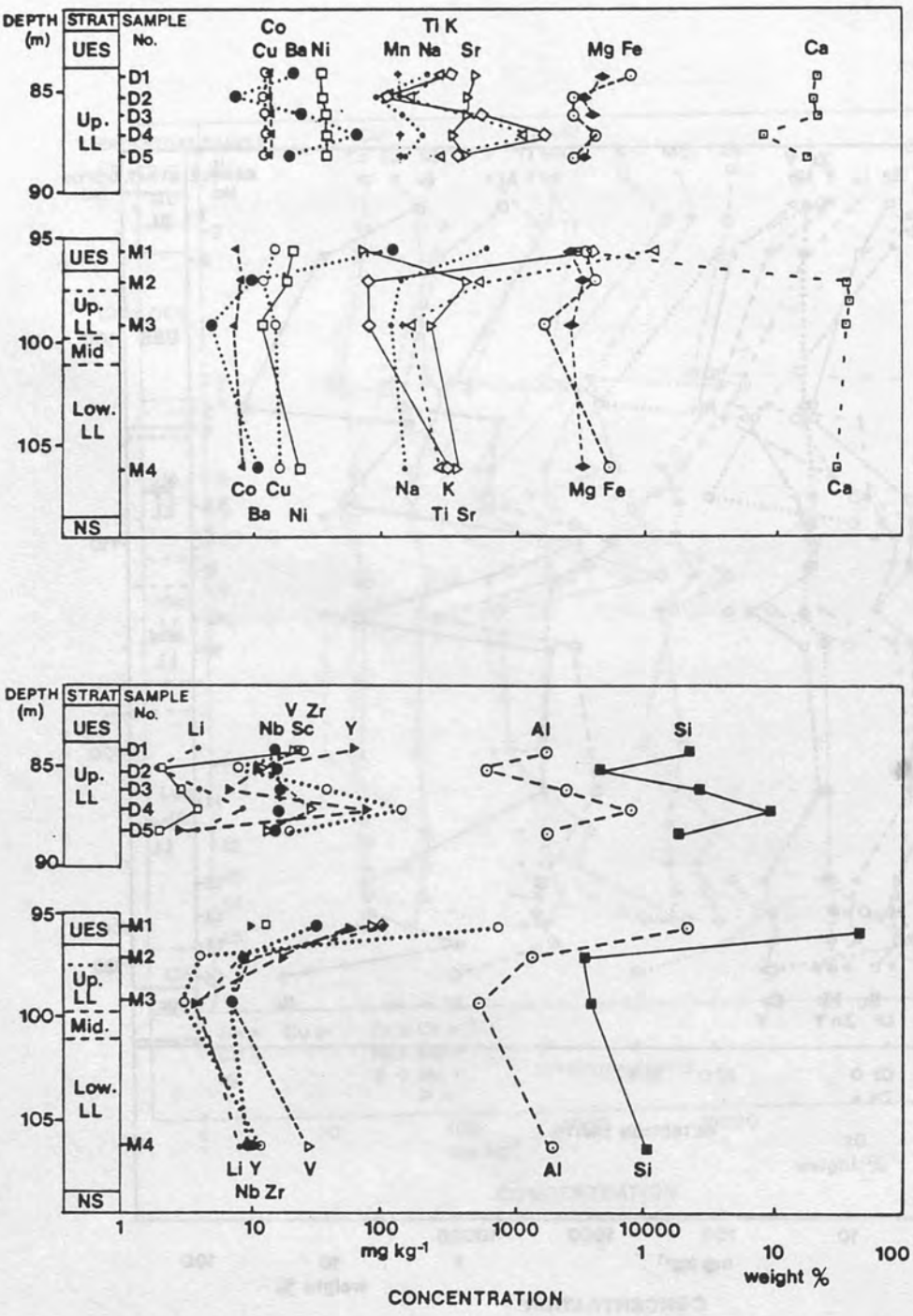


Figure 5.3

Major and trace element data for rock samples from Donington and Moulton West Fen boreholes plotted against depth. Detection limits and key as in figure 5.2.



Billingborough in the extreme north-west of the study area. Crushed core samples were centrifuged to extract interstitial water for analysis by BGS; subsequently the rock samples themselves were analysed for this study. A sequence of five samples from a depth of 29.3 m in the borehole were obtained. The top and bottom samples were close to fissures and were buff in colour; the three samples from between the fissures were of the unaltered grey limestone.

5.2.2 Results

Major and trace element analyses of the rock samples are presented in appendix 4 and figures 5.2 and 5.3. Major element data for silicate rocks are reported as oxides on a weight percent basis, therefore determinations for silicon, calcium, manganese, titanium, sodium, phosphorus and aluminium have been converted to elemental concentrations with working detection limits of 468, 145, 155, 120, 64, 44 and 43 mg kg^{-1} respectively. The remaining 16 elements have detection limits of 2 mg kg^{-1}, with the exceptions of 5 mg kg^{-1} for chromium, copper and zinc and 9 mg kg^{-1} for molybdenum (see 4.6). Rare earth element (REE) determinations are presented in tables 4.1A-4.4A for all samples from Bicker, Donington and Moulton West Fen, and two samples from the Billingborough borehole: BL3, a grey, unaltered limestone, and BL5, an altered buff sample adjacent to a fissure. The REE data are normalised to a standard shale in accordance with convention (Piper, 1974); a shaley sample would thus plot in a horizontal line. Shale normalised abundances for each sample are presented in figure 5.4.

The variable lithologies of the Lincolnshire Limestone are best reflected in the geochemical distributions of core from Bicker borehole (figures 5.2 and 5.4), as samples from the whole aquifer were analysed. The dominant elements are calcium in the limestone samples (Ca is equal to 40% in a pure limestone) and silicon in the

Figure 5.4

Shale-normalised plot of rare earth elements for rock samples from Bicker borehole (this page) and Moulton West Fen, Donington and Billingborough boreholes (facing page).

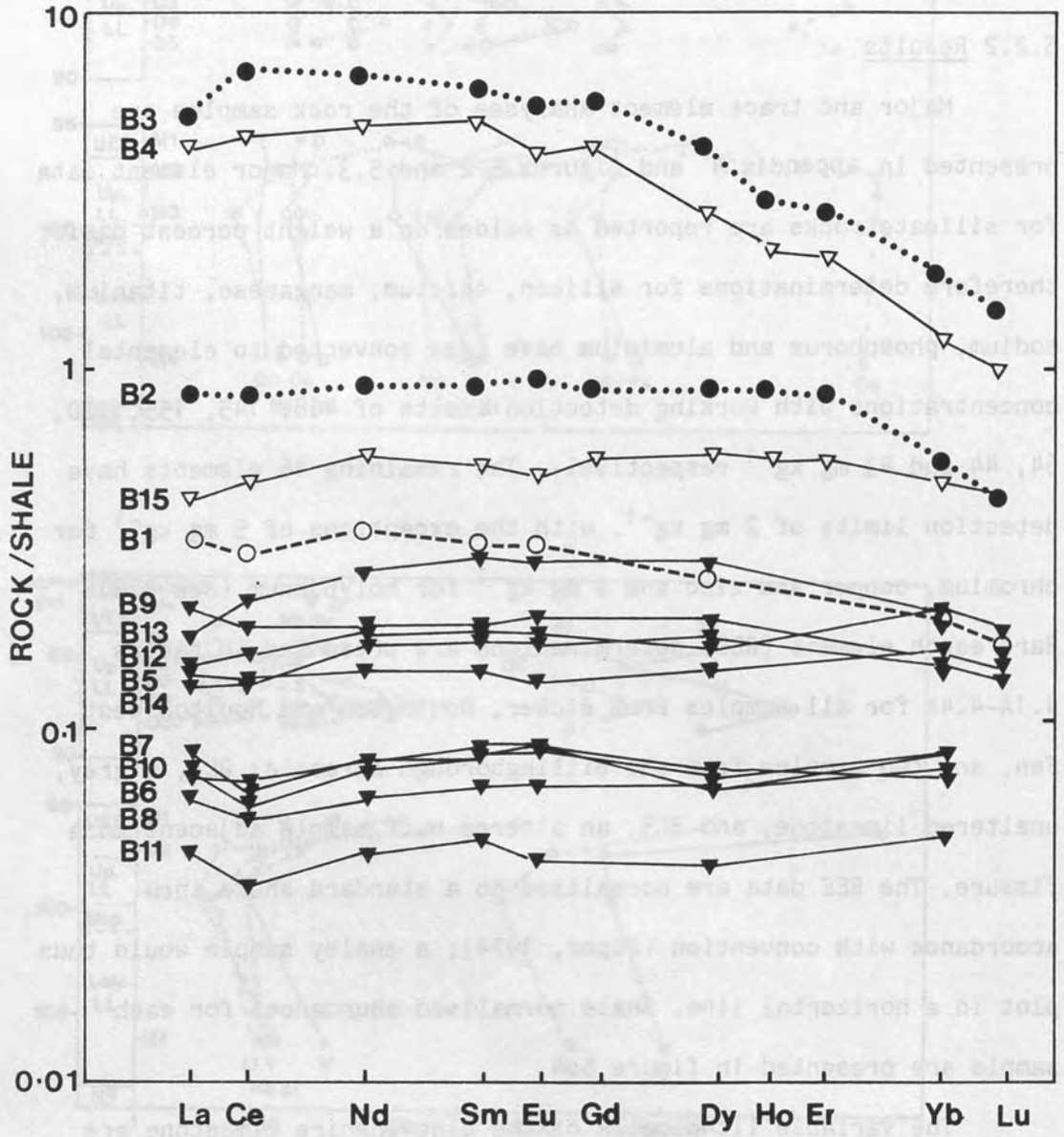
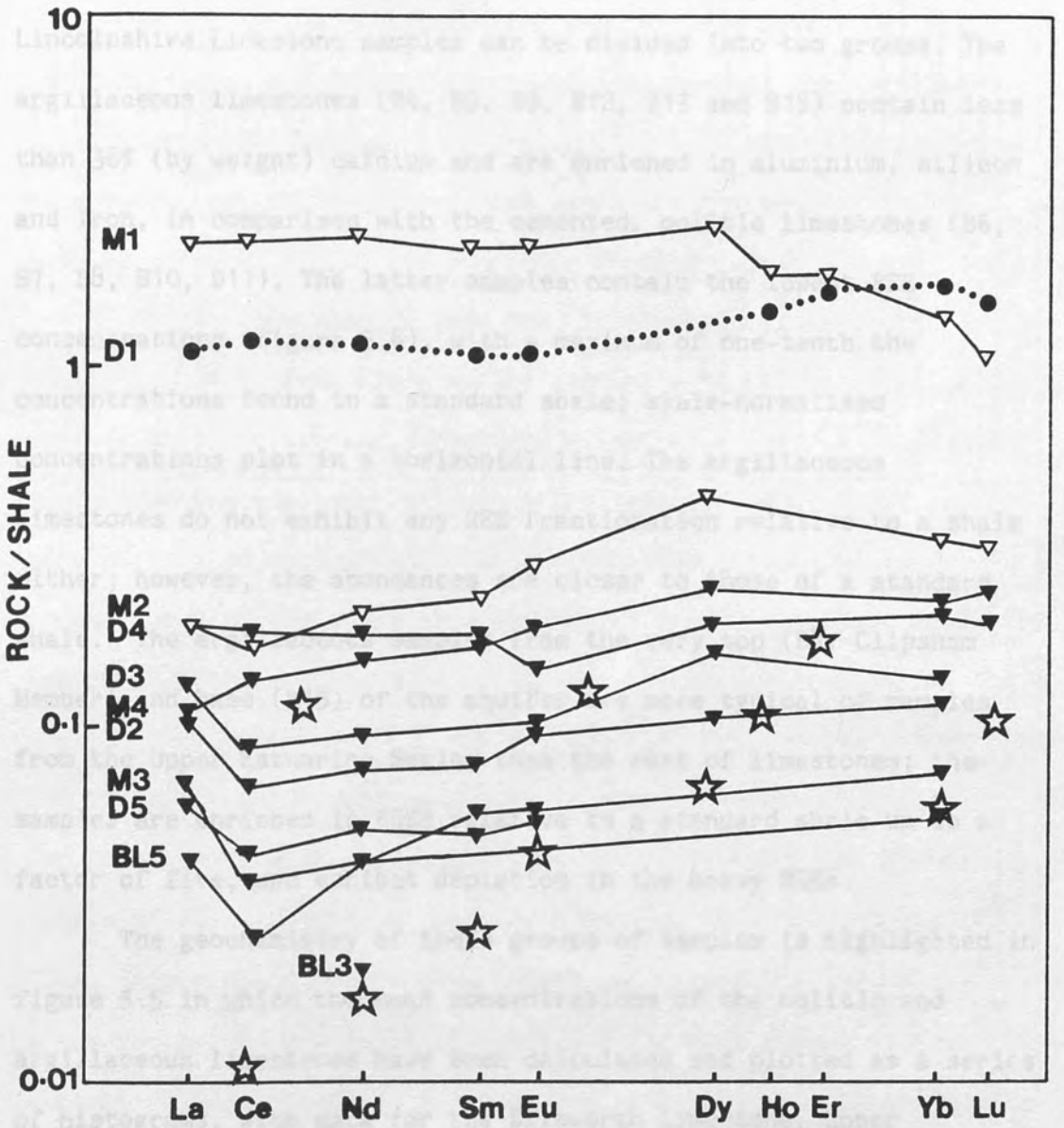


Figure 5.4 continued

Open circles = Blisworth Limestone, solid circles = Upper Estuarine Series, open triangles = top and basal Lincolnshire Limestone samples, solid triangles = Lincolnshire Limestone. Stars = shale-normalised detection limit for each determinand.



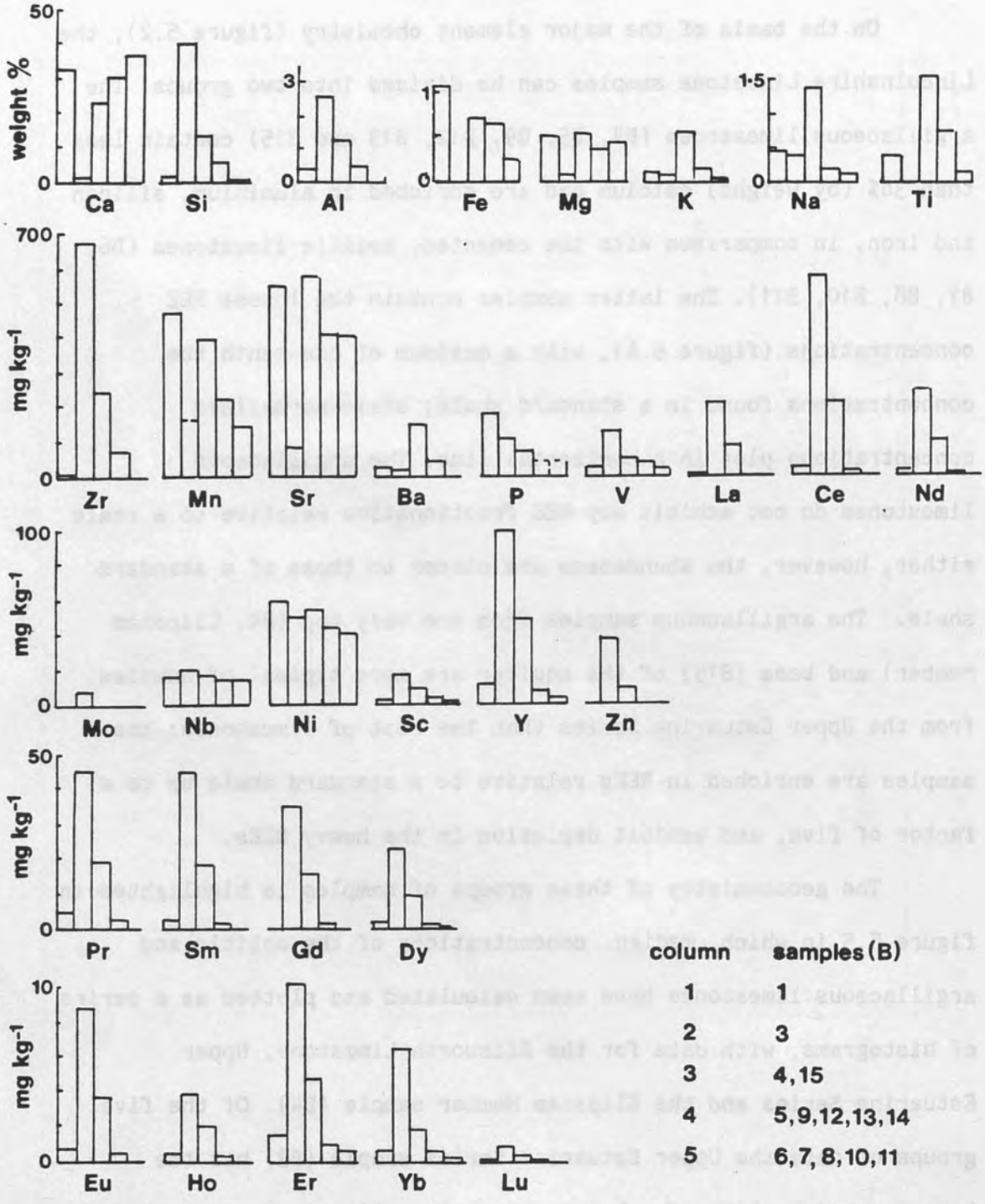
shales of the Upper Estuarine Series (Si = 40%). Sample B2 is from a shell bed from the top of the series; B3 typifies the silts and shales of the lower part of the Upper Estuarine Series, it is enriched in aluminium, zirconium and vanadium and depleted in calcium, magnesium, potassium, titanium, manganese and strontium, relative to most of the limestone samples.

On the basis of the major element chemistry (figure 5.2), the Lincolnshire Limestone samples can be divided into two groups. The argillaceous limestones (B4, B5, B9, B12, B13 and B15) contain less than 36% (by weight) calcium and are enriched in aluminium, silicon and iron, in comparison with the cemented, oolitic limestones (B6, B7, B8, B10, B11). The latter samples contain the lowest REE concentrations (figure 5.6), with a maximum of one-tenth the concentrations found in a standard shale; shale-normalised concentrations plot in a horizontal line. The argillaceous limestones do not exhibit any REE fractionation relative to a shale either; however, the abundances are closer to those of a standard shale. The argillaceous samples from the very top (B4, Clipsham Member) and base (B15) of the aquifer are more typical of samples from the Upper Estuarine Series than the rest of limestones; the samples are enriched in REEs relative to a standard shale up to a factor of five, and exhibit depletion in the heavy REEs.

The geochemistry of these groups of samples is highlighted in figure 5.5 in which the mean concentrations of the oolitic and argillaceous limestones have been calculated and plotted as a series of histograms, with data for the Blisworth Limestone, Upper Estuarine Series and the Clipsham Member sample (B4). Of the five groups of data the Upper Estuarine Series sample (B3) has the lowest concentration of calcium, magnesium, titanium, manganese and strontium and the highest concentration of silicon, aluminium,

Figure 5.5

Mean concentrations of argillaceous and oolitic limestones from the Lincolnshire Limestone and overlying lithologies. Columns 1 and 2 represent samples from the Blisworth Limestone and Upper Estuarine Series; columns 3 and 4 are argillaceous limestones from the Lincolnshire Limestone, from the top and base (column 3) and from the main body of the aquifer (column 4). Median concentrations of carbonate-cemented oolitic limestones are presented in column 5.



zirconium, vanadium, molybdenum, niobium, scandium, yttrium, zinc and all the REEs. The purest limestones have the highest calcium content and the lowest abundance of all other elements, with the exception of magnesium and strontium. The two limestone samples from the top and base of the aquifer (B4 and B15) have the lowest calcium values of the limestones (31%) but contain the highest concentrations of iron, magnesium, potassium, sodium, titanium, strontium and barium of all fifteen samples, and only lower REE abundances than the Upper Estuarine Series sample. The argillaceous limestones in the main part of the aquifer plot midway between the mean concentrations for the purest limestone members and the two samples in contact with the confining formations, B4 and B15.

Of the five samples from the Lincolnshire Limestone at Donington, D1 is from close to the contact with the Upper Estuarine Series. As a shelly sample from the Clipsham Member, it has a much higher calcium and lower silicon value than its counterpart at Bicker, it also demonstrates considerable REE enrichment in comparison with the other samples; D2, D3 and D5 correlate well with the purer oolitic limestones of Bicker, while D4 is typical of the argillaceous limestones. Of the Moulton West Fen samples, M1 is from the Upper Estuarine Series; the shale normalised REE distribution for this sample plots differently to the Upper Estuarine Series sample of Bicker borehole, showing a gradual enrichment in heavy REEs. Sample M3 is a very pure limestone, having a shale-normalised abundance of below 0.1 for most elements, a silicon content of less than 0.5% and a slight enrichment in potassium only.

The five grey and buff limestone samples from the Billingborough borehole do not show any systematic variation that could reflect the alteration of samples BL3 and BL5 in any way. The rare earth element content is very low, being below the working

Table 5.1

Major phases in argillaceous samples from the Linconshire Limestone (LL) and Upper Estuarine Series (UES) from Bicker borehole.

Sample	B3	B4	B14
$CaCO_3$	0.5	36.6	48.5
$CaSO_4.2H_2O$	2.6	74	38.7
SiO_2 + Al_2O_3	94	6	11
H_2O in gypsum	0.5	15.5	10.2
Total (minus water)	97%	101%	98%
Stratigraphy	UES	Upper LL (Clipsham Mbr)	Lower LL (Greetwell Mbr)
Lithology	Shale with plant fragments + rootlets	gypsiferous carbonate with clay lenses	Oolite with clay lenses

detection limit for most elements; the lanthanum, cerium and neodymium determinations indicate however, that the grey, unaltered sample (BL3) is slightly purer than the buff, oxidised rock; the unaltered core also has a slightly lower calcium and higher silicon value.

It was not possible to determine the sulphur content of the samples, due to the problem of volatilisation during sample preparation; however, gypsum was identified by XRD in all but the purest limestones. The acid-soluble content of B3, B4 and B14 was 0.32, 46 and 63% respectively, therefore an upper limit for the amount of calcium bound up in carbonate was ascertained. Assuming that the rest of the calcium occurred as sulphate, the concentration of gypsum in these samples was estimated at approximately 3, 74 and 39% and therefore sulphur concentrations of the order of 0.5, 14 and 9% are plausible in B3 (Upper Estuarine Series), B4 (Clipsham Member) and B13 (oolite with clay lenses), respectively (table 5.1). These values refer to sulphur present as sulphate only and are considerably higher than the average content reported in carbonates (0.46%) and argillaceous rocks (0.19% sulphur), (Matthess, 1982), although the gypsum content of the purer oolitic limestones is minimal.

A qualitative XRD investigation of the mineralogy of the non-carbonate portion of the samples revealed the presence of abundant quartz and kaolinite, and minor amounts of illite, smectite and alkali feldspar.

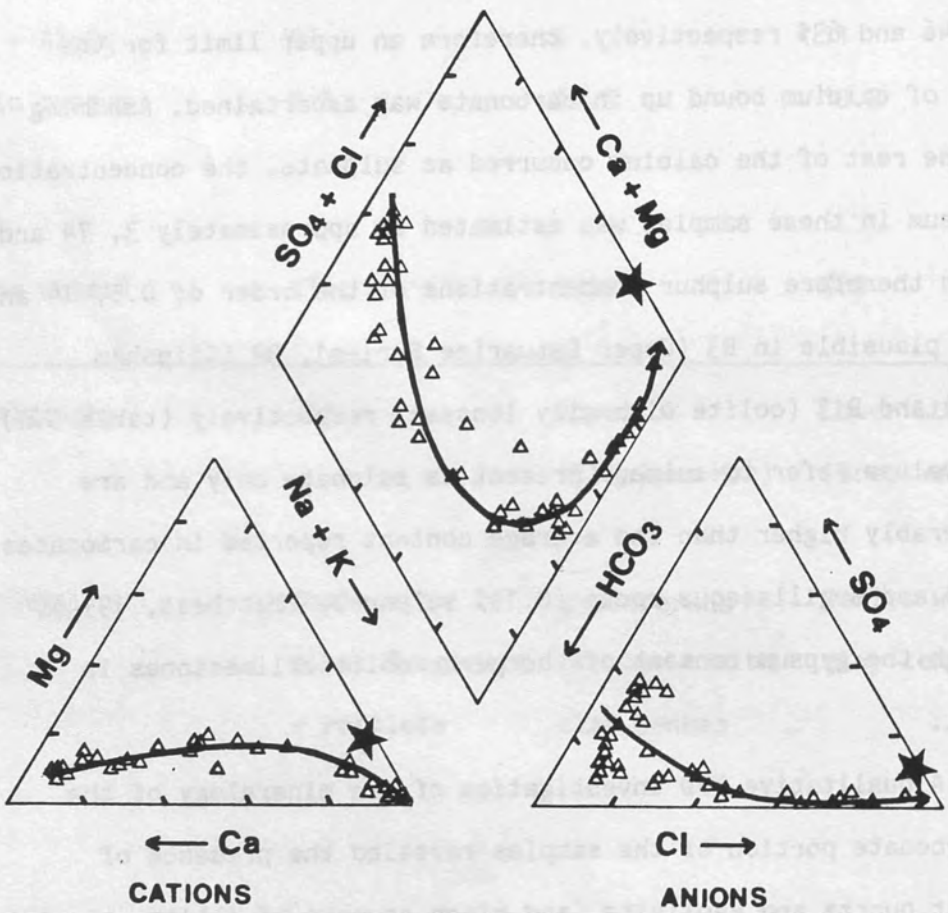
5.3 GROUNDWATER SAMPLES

5.3.1 Borehole locations

Groundwaters sampled in December 1985 were collected from the boreholes indicated in figure 5.1. The midpoint of the aquifer intersects the most westerly boreholes (15 km from outcrop) at

Figure 5.6

Trilinear (Piper) diagram for Lincolnshire limestone groundwaters. Major ions (meq/l) are plotted as a percentage of total cations or anions, graduations are in 20% increments. Arrows indicate general direction of groundwater flow and the sample represented by a star is seawater from The Wash.



20-30 m B.O.D and at 95-110 m, 30 km from outcrop. Spatial trends are identfied below and discussed in section 6.3.

The aquifer is confined throughout the sampling area. In general, artesian conditions predominate, with the potentiometric surface being approximately 10 m above ground level. In the western part of the area, towards the unconfined section of the aquifer, subartesian conditions occur in autumn/winter, following periods of low recharge; hence in December 1985, groundwater could only be obtained at Klondyke Stud Farm, Bourne (sample 6), by pumping the water to the surface, while other sites close to Eastings 10 and 11 without pumping facilities, could not be sampled, for example around TF1029.

Boreholes maintained by Anglian Water for groundwater observation, are steel-lined and often contain small diameter sample tubes to facilitate efficient flushing of the borehole and rapid access to fresh groundwater samples from the aquifer itself. The private boreholes in the area are also mostly steel-cased, although some very old holes may be iron-lined (M. Gibb, *pers. comm.*, 1986). No boreholes in the sampling area are lined with synthetic materials.

5.3.2 Results

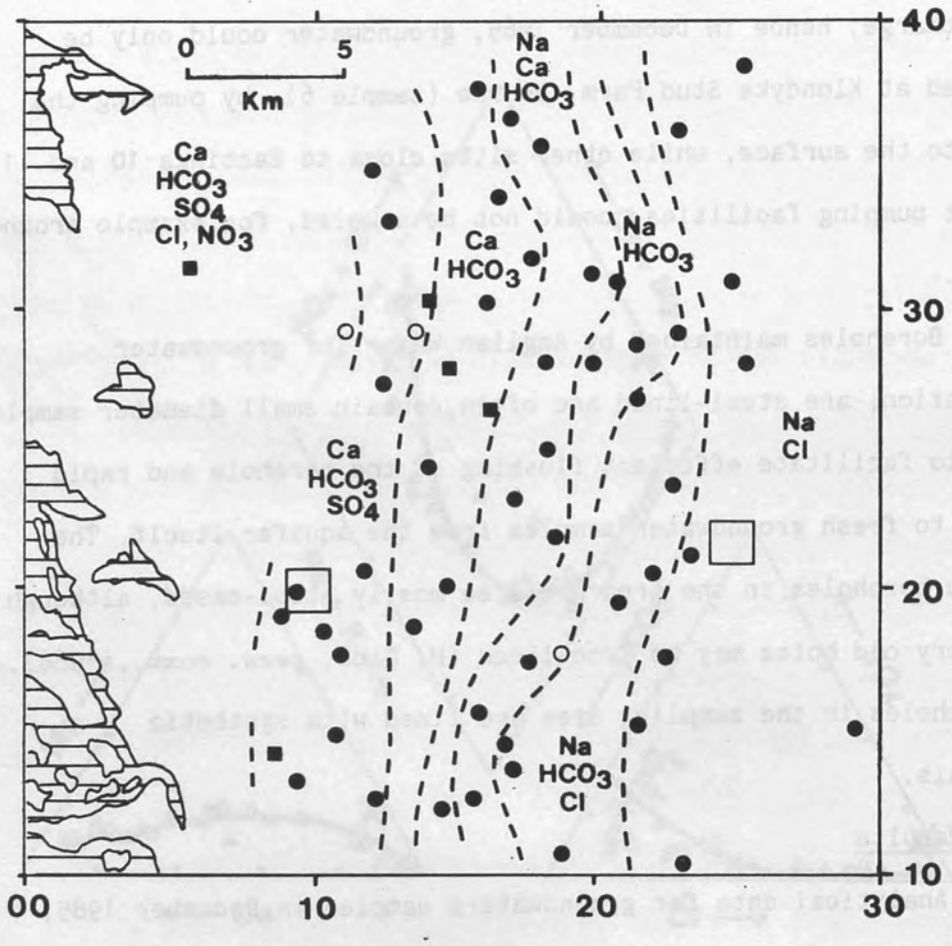
Analytical data for groundwaters sampled in December 1985, are presented in table 5.1A. Many of the trace elements occur at levels below the LQDC (4.6) therefore only 'less than' values are reported.

5.3.2.1 Classification according to major ion predominance

Major ions (as milliequivalents) are plotted as percentages of total cations or anions, in a Piper diagram (figure 5.6), which demonstrates a chemical trend between calcium-bicarbonate and sodium chloride end-members; from the diagram, each sample has been

Figure 5.7

Major ion zones in the Lincolnshire Limestone groundwaters. Solid circles = groundwaters samples in December 1985, open circles = sample collected and analysed prior to December 1985, solid squares = primary public supply abstraction sites.



classified according to major ion predominance, and plotted as a series of chemical zones across the sampling area (figure 5.7).

5.3.2.2 Absolute Concentrations

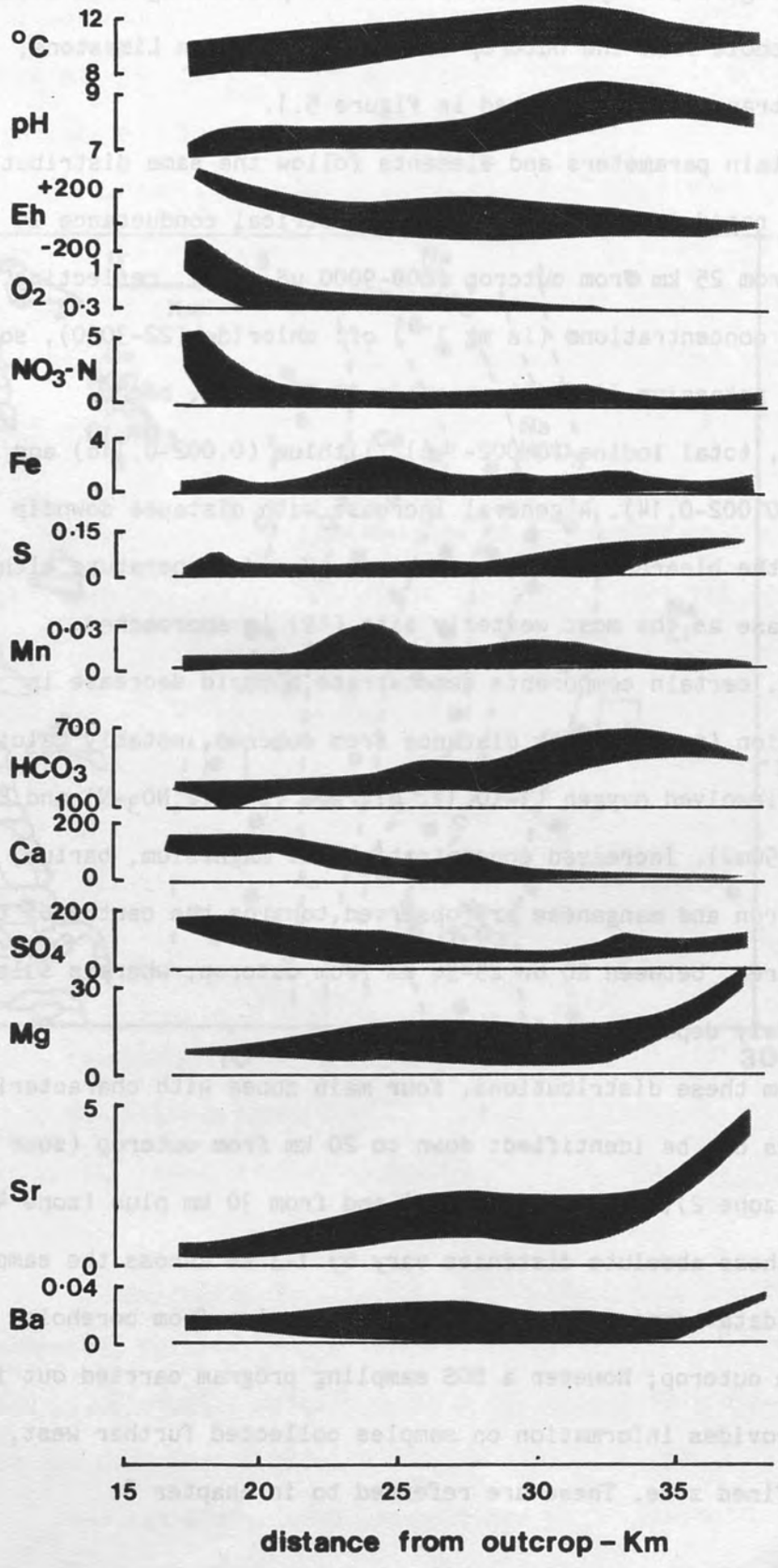
In figure 5.8 hydrochemical data are plotted against distance of the borehole from the outcrop of the Lincolnshire Limestone, using the transect demonstrated in figure 5.1.

Certain parameters and elements follow the same distribution closely. A rapid increase in specific electrical conductance is observed from 25 km from outcrop (800-9000 uS cm^{-1}), reflecting the increasing concentrations (in mg l^{-1}) of: chloride (22-3000), sodium (15-2000), potassium (1.6-12), bromide (0.06-15.5), boron (0.03-3.3), total iodine (0.002-1.6), lithium (0.002-0.116) and sulphide (0.002-0.14). A general increase with distance downdip is noted for the bicarbonate concentration, pH and temperature although they decrease as the most westerly site (49) is approached. Conversely, certain components demonstrate a rapid decrease in concentration (mg l^{-1}) with distance from outcrop, notably calcium (160-5), dissolved oxygen (1-<0.1), nitrate (5-<0.2 NO_3-N) and Eh (300 to -150mV). Increased concentrations of magnesium, barium, silicon, iron and manganese are observed towards the centre of the sampling area, between 20 or 25-30 km from outcrop, whereas sulphate is relatively depleted in this area.

From these distributions, four main zones with characteristic chemistries can be identified: down to 20 km from outcrop (zone 1); 20-25 km (zone 2); 25-30 km (zone 3) and from 30 km plus (zone 4), although these absolute distances vary by 1-3 km across the sampling area. The data commence with groundwater samples from boreholes 15 km from outcrop; however a BGS sampling program carried out in 1982-83 provides information on samples collected further west, in the unconfined zone. These are referred to in chapter 6.

Figure 5.8

Spatial distribution of various parameters in the Lincolnshire Limestone groundwaters. Distances are along the transect indicated in figure 5.1.



Units of concentration: mg l^{-1}

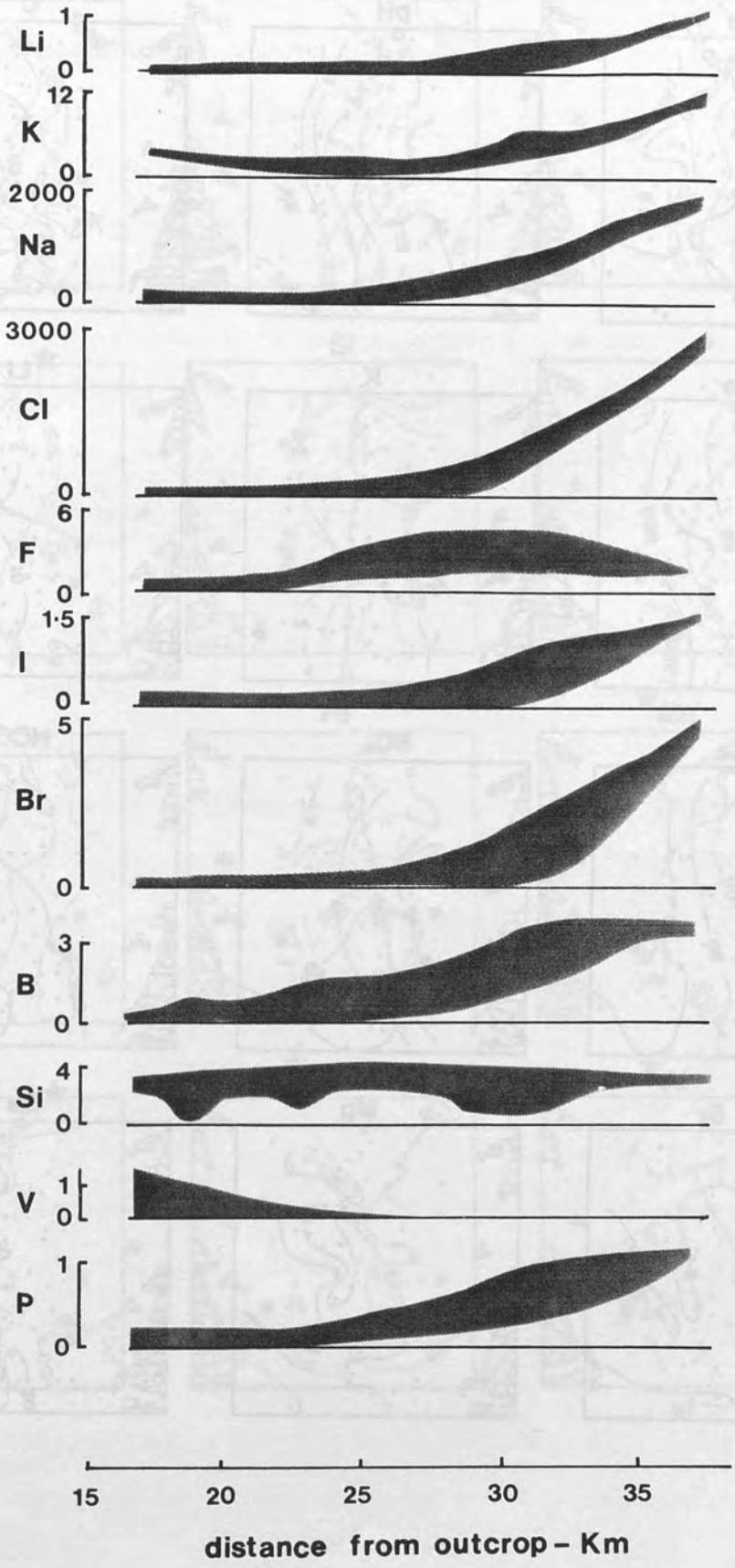


Figure 5.9

Contoured plots of various parameters in the Lincolnshire Limestone groundwaters
Concentration units: mg l^{-1}

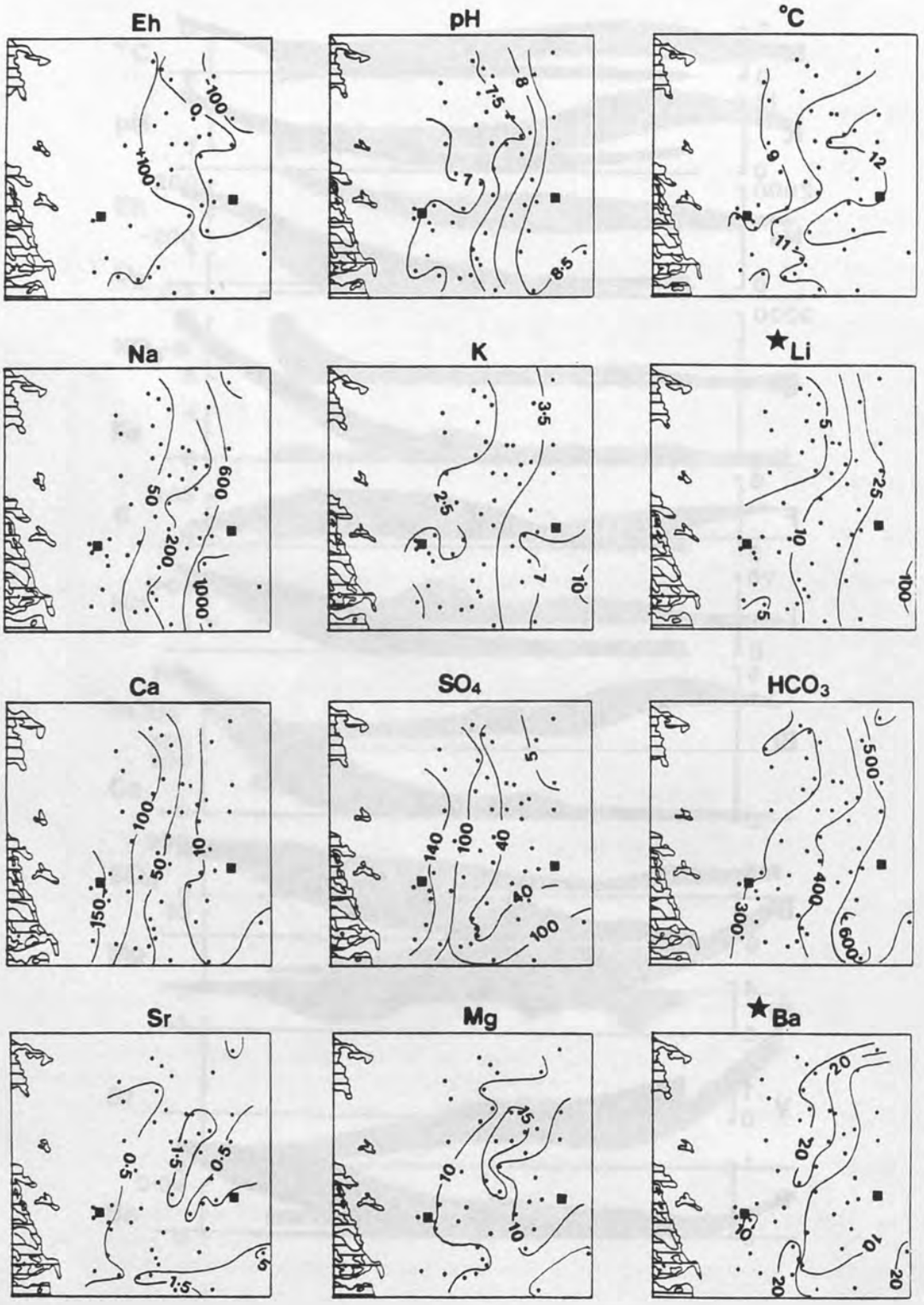
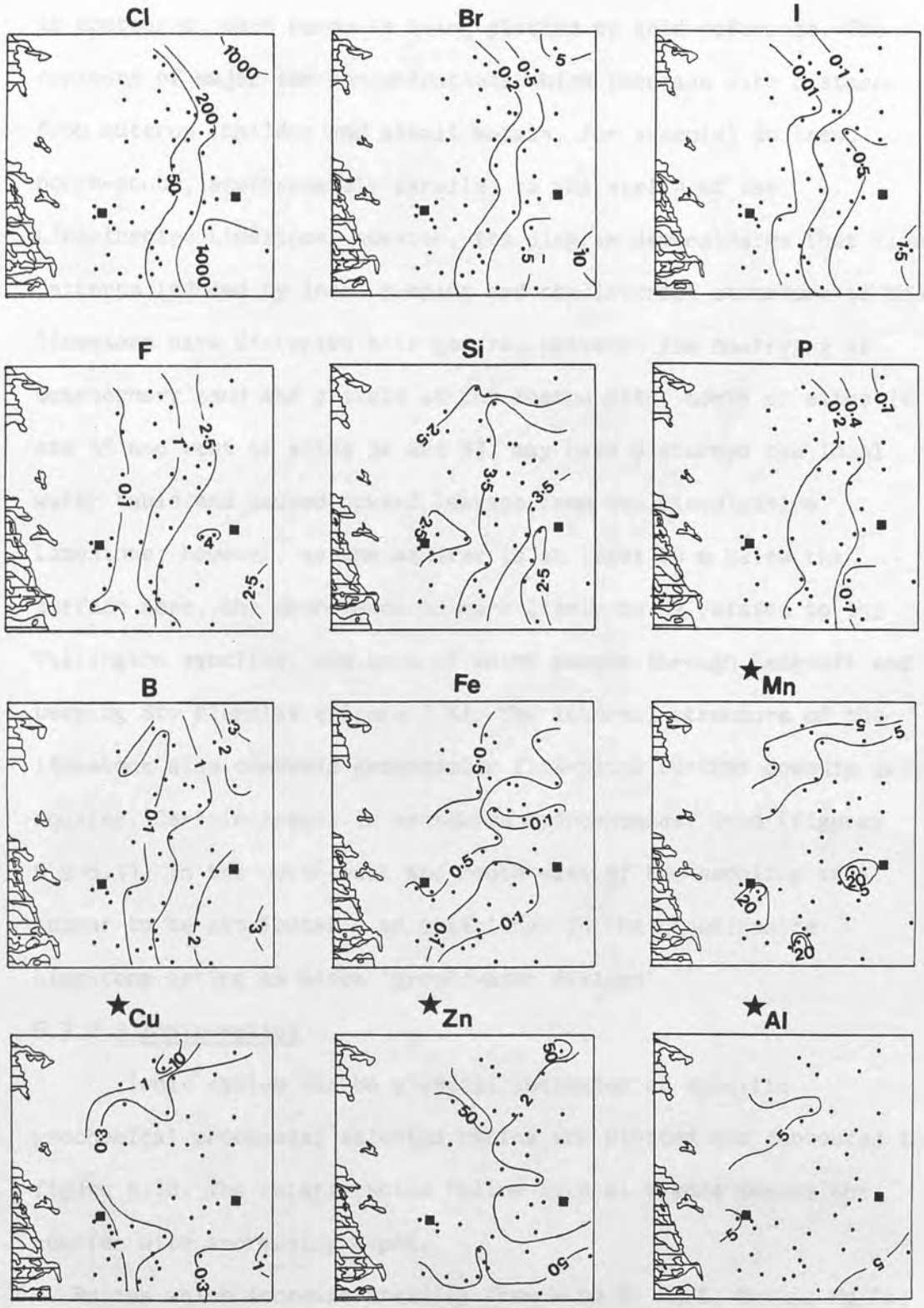


Figure 5.9 contd.

Asterisks denote concentration units of $\mu g\ l^{-1}$.



A considerable degree of scatter is seen in some of the plots due to the size of the sampling area. A more detailed picture of the spatial hydrogeochemistry is presented in figure 5.9, where data is contoured, each borehole being plotted by grid-reference. The contours of major ion concentrations which increase with distance from outcrop (halides and alkali metals, for example) do trend north-south, approximately parallel to the strike of the Lincolnshire Limestone; however, the diagram demonstrates that flow patterns induced by local pumping and the internal structure of the limestone have disrupted this general pattern. The quarrying of Quarternary sand and gravels at the Baston pits, north of sites 34 and 35 and west of sites 32 and 33, may have disturbed the local water table and caused upward leakage from the Lincolnshire Limestone; however, as the aquifer is at least 20 m below the surface here, the phenomenon is more likely to be related to the Tallington syncline, the axis of which passes through Langtoft and Deeping St. Nicholas (figure 1.5). The internal structure of the limestone also controls groundwater flow-paths further downdip in the aquifer. Certain trends in contoured hydrochemical data (figures 5.9-5.11) in the north-east and south-east of the sampling area appear to be attributable to anticlines in the Lincolnshire Limestone acting as minor 'groundwater divides'.

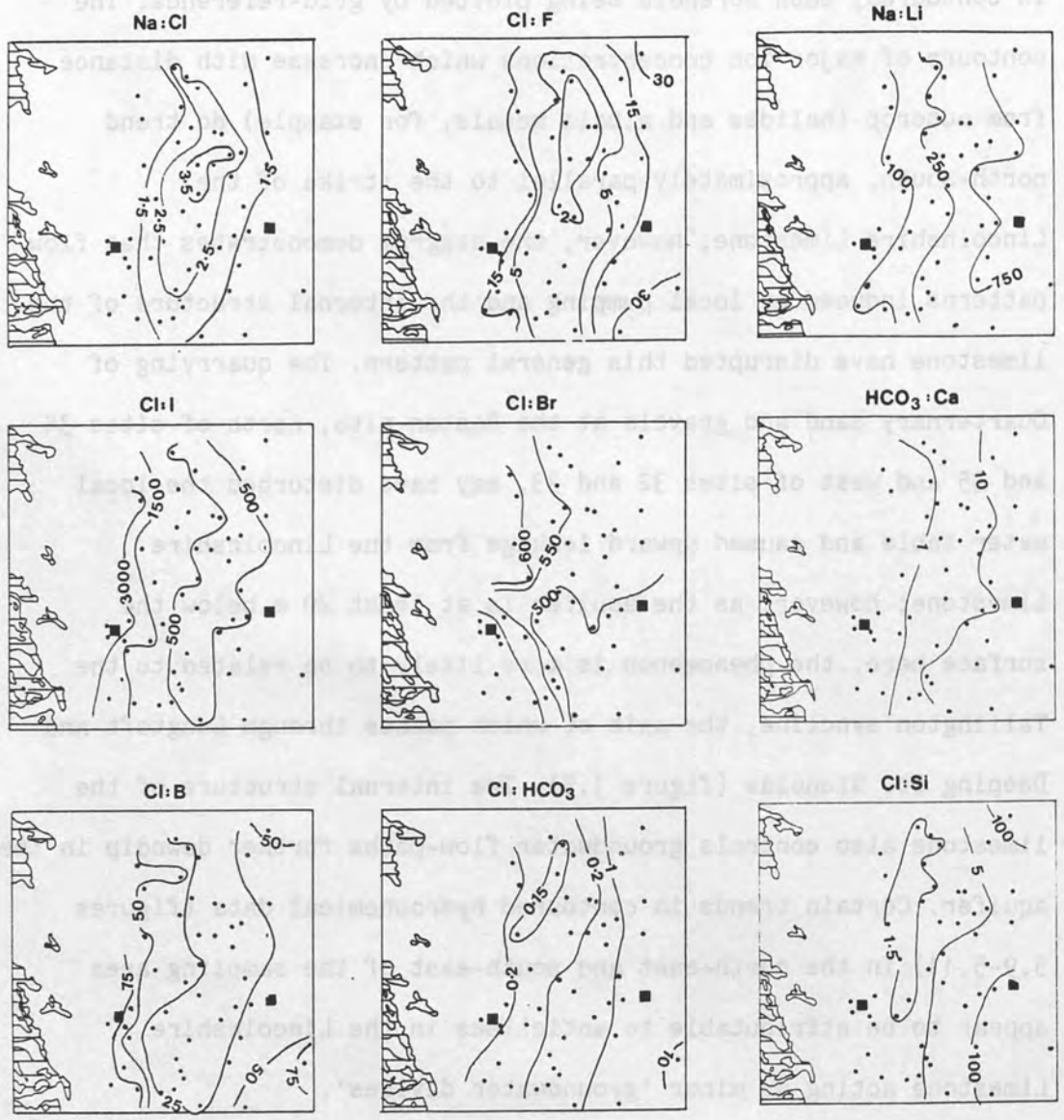
5.3.2.3 Ionic ratios

Ionic ratios can be a useful indicator of specific geochemical processes; selected ratios are plotted and contoured in figure 5.10. The relationships follow several trends across the aquifer with increasing depth.

1. Ratios which increase steadily from W to E: Na/K; Na/Li; Mg/Ca; Ba/Ca; SO_4/Ca; Sr/Ca; Sr/Mg; HCO_3/SO_4; Cl/HCO_3 and Cl/SO_4.
2. Ratios which increase by at least one order of magnitude:

Figure 5.10

Contoured plots of ionic ratios in the Lincolnshire Limestone groundwaters.



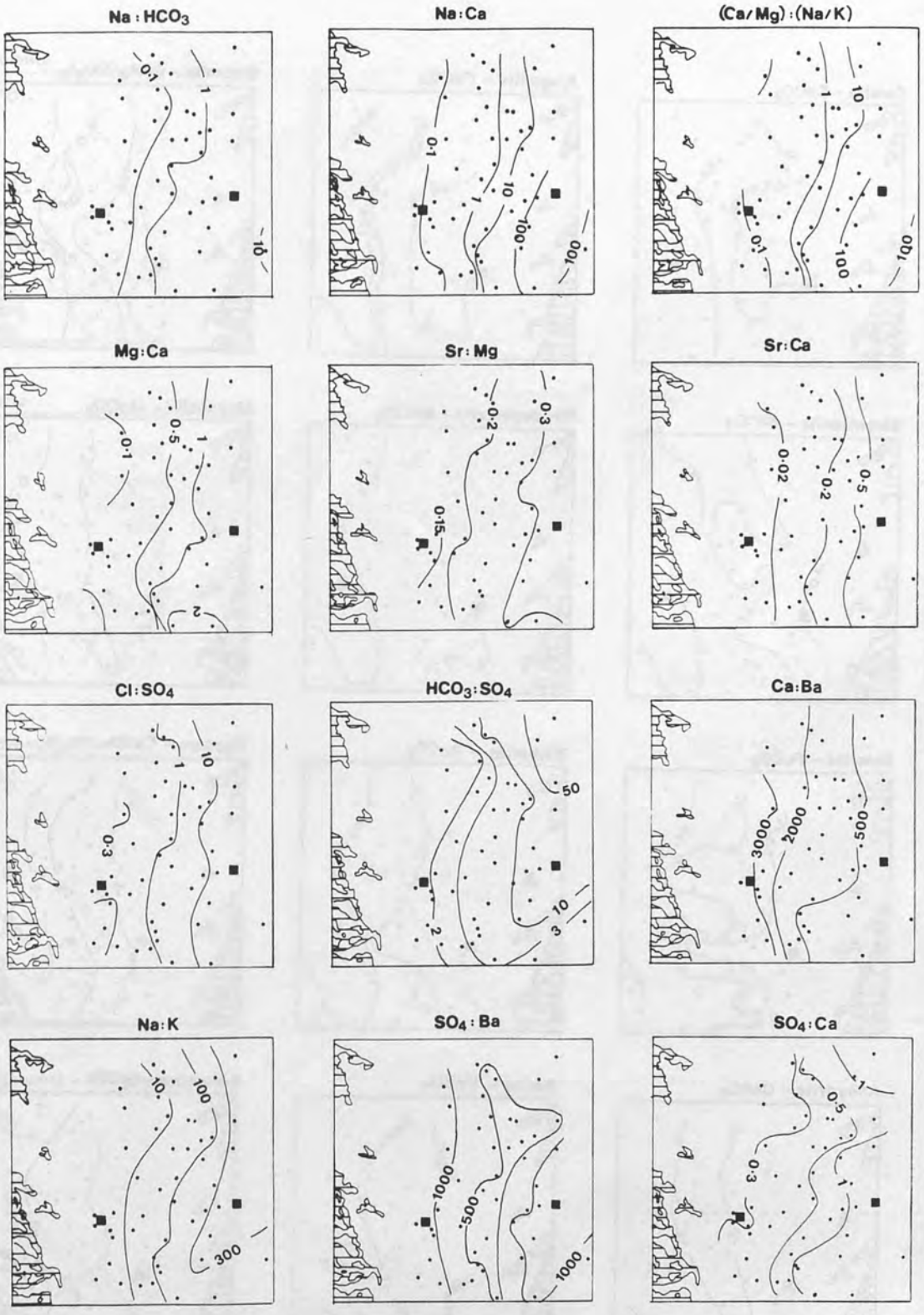
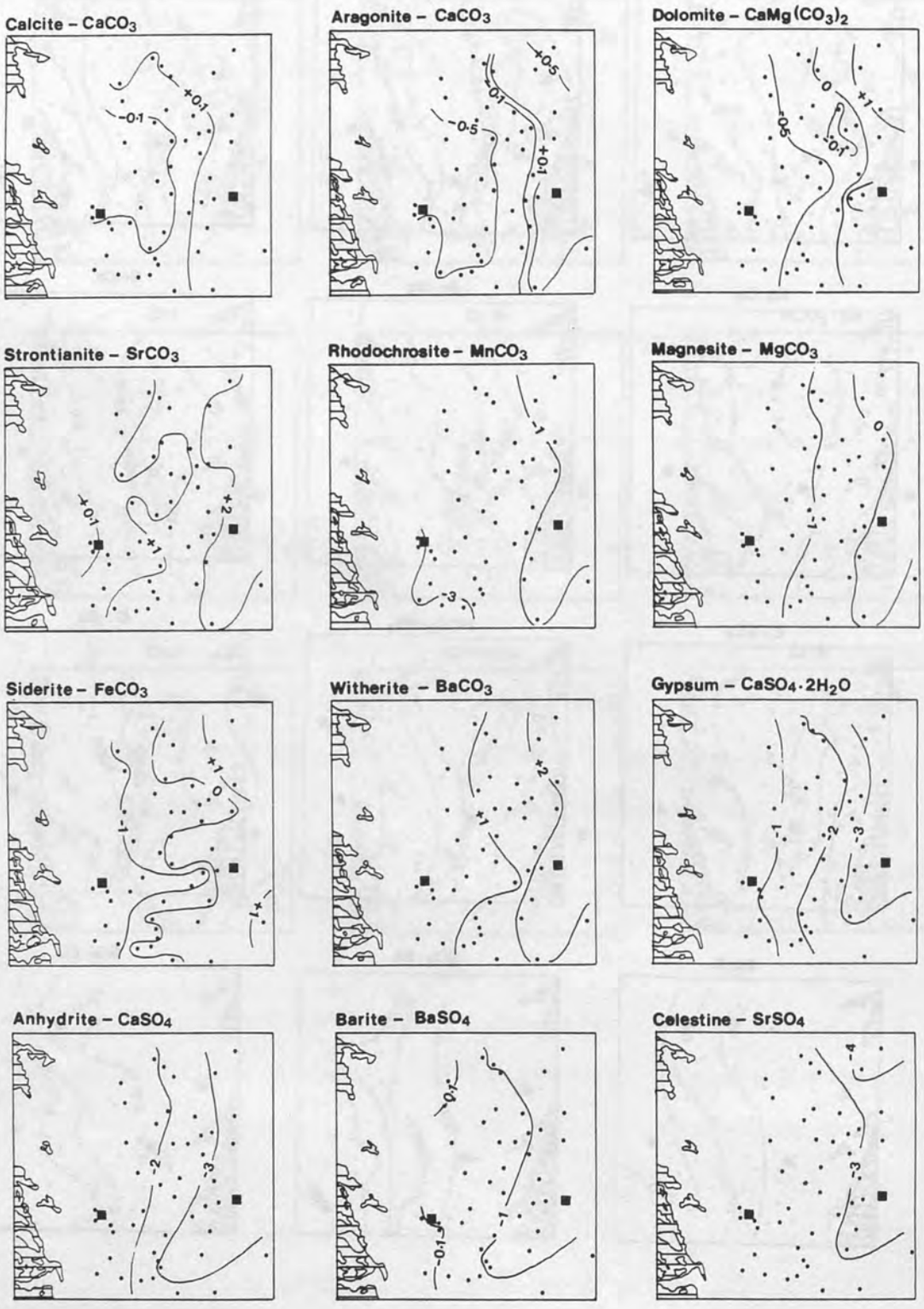
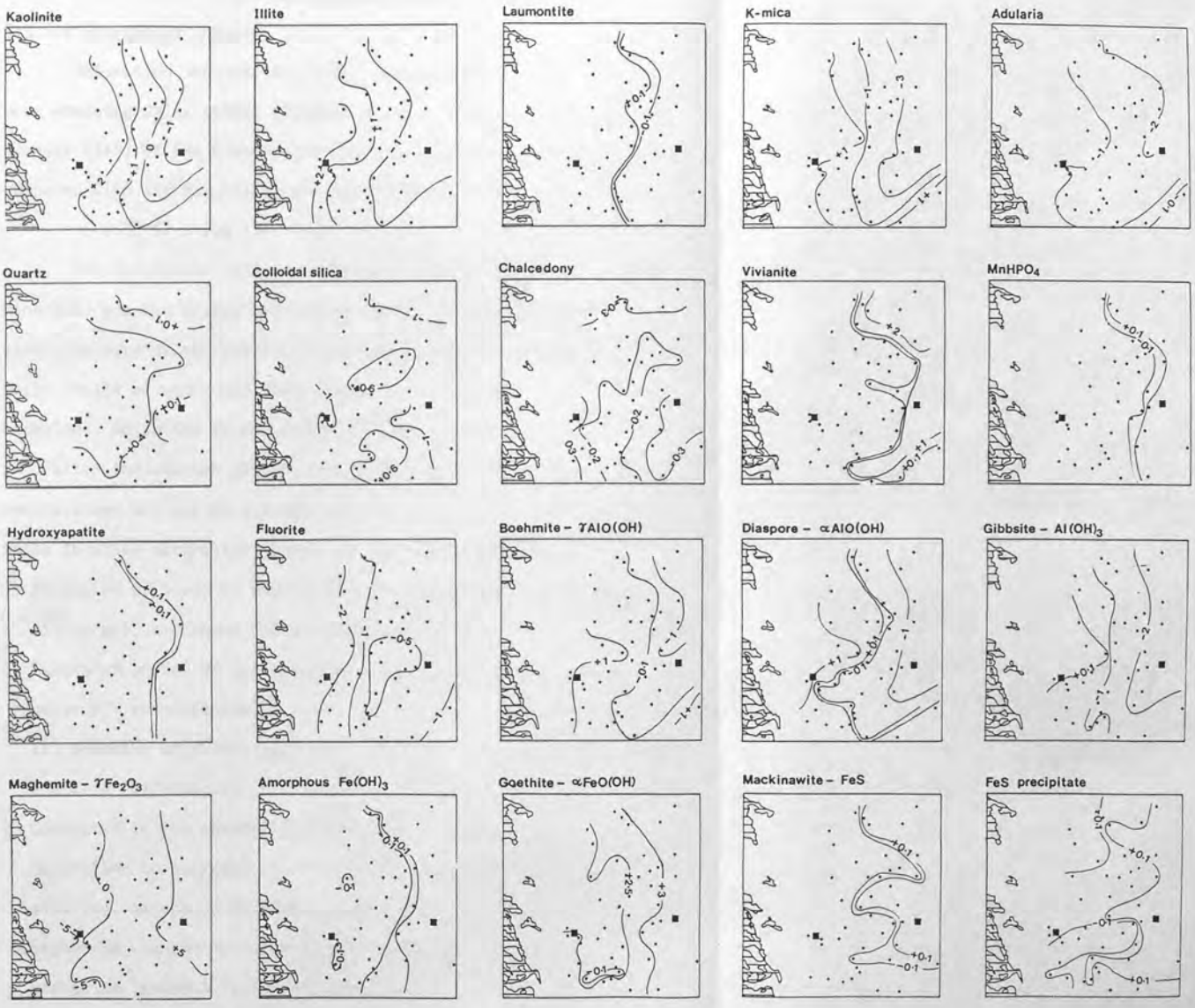

(Ca/Mg):(Na/K)
Na:Ca
Na:HCO3
Sr:Ca
Sr:Mg
Mg:Ca
Ca:Ba
HCO3:SO4
Cl:SO4
SO4:Ca
SO4:Ba
Na:K

Figure 5.11

Contoured plots of saturation indices in the Lincolnshire Limestone groundwaters.




Kaolinite
Illite
Laumontite
K-mica
Adularia
Quartz
Colloidal silica
Chalcedony
Vivianite
$MnHPO_4$
Hydroxyapatite
Fluorite
Boehmite – $\gamma AlO(OH)$
Diaspore – $\alpha AlO(OH)$
Gibbsite – $Al(OH)_3$
Maghemite – γFe_2O_3
Amorphous $Fe(OH)_3$
Goethite – $\alpha FeO(OH)$
Mackinawite – FeS
FeS precipitate

Na/HCO_3, Na/Ca; HCO_3/Ca; Cl/Si and [(Ca+Mg)/(Na+K)].

3. Ion ratios which attain their maximum concentrations in a central N-S trending zone only: Na/Cl; B/Cl; F/Cl; I/Cl and Ba/SO_4.
4. Ion ratios which remain approximately constant: Br/Cl

5.3.2.4 Saturation indices

Saturation indices (S.I.) for various major mineral phases were computed using WATEQF (Plummer *et al.*, 1976); the ion activity product (IAP) of the dissolved constituents of the solid species is compared with its solubility product according to:

$$SI = \log (IAP/K_{SP})$$

The saturation indices of the carbonates, sulphates and clay minerals, and the oxides and hydroxides of iron, manganese and aluminium were of the greatest interest as possible controls for the solubilities of major and minor elements in the Lincolnshire Limestone. While the value of many of these may be marginal, the saturation indices are plotted and contoured in fig. 5.11 for completeness and can be divided into six main trends relating to the zones in which saturation, under- or oversaturation dominates.

1. Saturated or close to saturation over much of the area: calcite, silica gel, amorphous FeS precipitate
2. Saturated in the W: (a) becoming oversaturated with distance from outcrop - strontianite;
   (b) becoming undersaturated with distance - gibbsite, barite and adularia (K-feldspar)
3. Saturated in the central N-S zone: (a) W-E trend from under-saturation to oversaturation: calcite, aragonite, dolomite, siderite, amorphous FeS precipitate, mackinawite (FeS), maghemite, amorphous $Fe(OH)_3$, hydroxyapatite, $MnHPO_4$ and vivianite (hydrous ferrous phosphate),
   (b) W-E trend from oversaturation to undersaturation: kaolinite,

illite, K-mica, laumontite (zeolite), diaspore, boehmite

4. Approaching/attaining saturation in the E: fluorite, rhodochrosite, magnesite, quartz
5. Increasing undersaturation in the E: gypsum, anhydrite, celestine, amorphous $Al(OH)_3$
6. Increasing supersaturation in the E: witherite, goethite

5.4 SUMMARY

The rocks of the Lincolnshire Limestone aquifer exhibit widely varying lithologies and chemistries. The purest oolitic limestones contain calcium equivalent to 90-95% $CaCO_3$, with REE contents less than 0.1 times that of a standard shale. By comparison, samples from the Clipsham Member at the top of the aquifer are relatively enriched in iron, magnesium, potassium, sodium, titanium, strontium, barium and the REEs. The aquifer is confined from above by the Upper Estuarine Series, which, with the exception of a shell bed, has a lower calcium content than any of the argillaceous beds in the Lincolnshire Limestone formation. It contains the highest concentrations of silicon, aluminium, zirconium, vanadium, molybdenum, niobium, scandium and yttrium and the REE content is up to five times greater than that of a standard shale.

Figure 5.7 illustrates the change in major ion chemistry of the groundwater with its passage downdip; the groundwater nearest the Lincolnshire Limestone outcrop is calcium-sulphate-bicarbonate type, in the east sodium and chloride are dominant. Four main chemical zones in the groundwaters can be identified and trends in the most significant parameters are:

Zone 1: 15-20 km from outcrop

Decreasing: Ca, SO_4 and V

Constant: Na, K, Cl, Br, I, Ba and S

Increasing: pH, HCO_3, Mg, Sr, B and F

Decreasing: Eh, O_2 and NO_3

Zone 2: 20-25 km from outcrop

Sharp decrease: Ca, SO_4 and V

Sharp decrease: O_2 and NO_3 (< detection limit) and Eh

Maximum concentration of Fe and Mn

Increasing: Na

Zone 3: 25-30 km from outcrop

Decreasing: Mg, Sr and Ba

Slower decrease/levelling off: Eh, O_2, Ca, SO_4 and V

Sharp increase: Na, Cl, HCO_3, I, Br, P and B

Gradual increase: pH, temperature and Li

Zone 4: 30 km from outcrop continuing eastwards

Rapid increase: Na, K, Li, Cl, I, Br, Mg, Sr, Ba, S and P

These zones are based on the distance of boreholes from outcrop when extrapolated onto a transect (figure 5.1); their boundaries are more rigorously delineated in chapter 6.

CHAPTER SIX

6: HYDROCHEMISTRY OF THE SOUTHERN LINCOLNSHIRE LIMESTONE

6.1 Introduction

The general geochemistry of the Lincolnshire Limestone and broad hydrochemical trends in its groundwaters have been presented in chapter 5. Controls on the mobility and occurrence of minor and trace elements in the waters are discussed and include carbonate equilibria, ion exchange, mixing between recharge and saline interstitial waters, redox controls, bacterial activity, adsorption, solubility controls and geochemical abundance. Temporal trends are also described in the light of previous research in the area.

6.2 ROCK SAMPLES

6.2.1 Influence of lithology on geochemistry

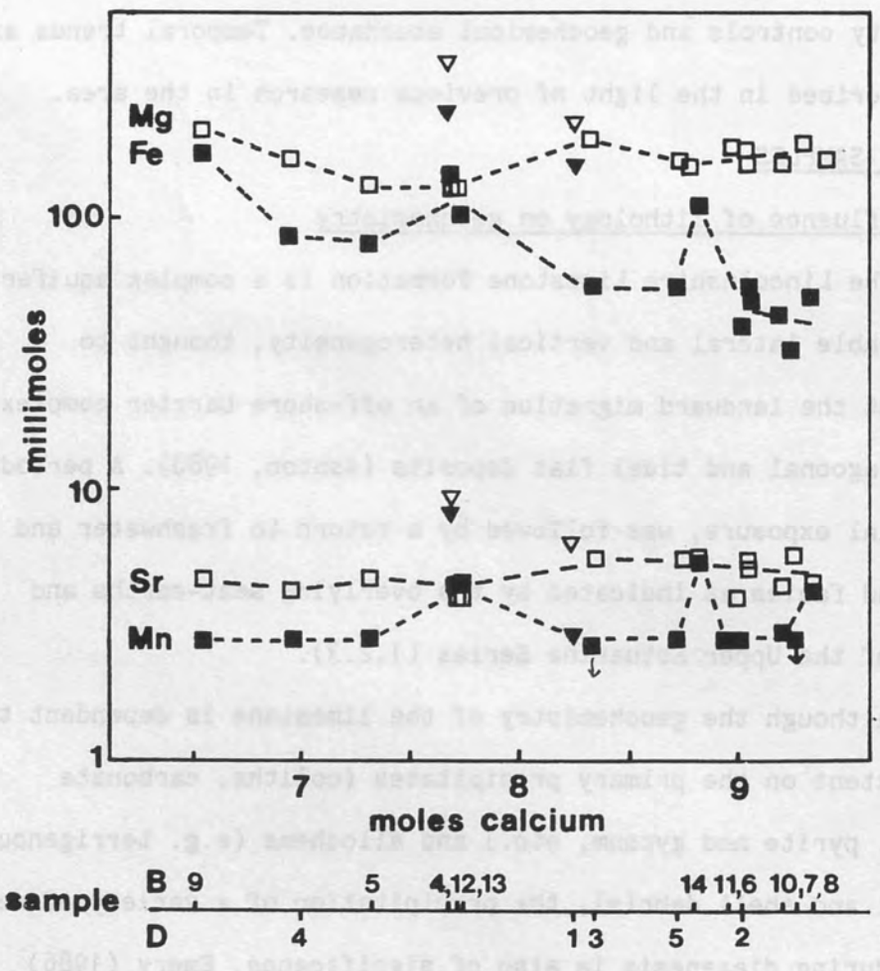
The Lincolnshire Limestone Formation is a complex aquifer of considerable lateral and vertical heterogeneity, thought to represent the landward migration of an off-shore barrier complex across lagoonal and tidal flat deposits (Ashton, 1980). A period of sub-aerial exposure, was followed by a return to freshwater and marshland facies as indicated by the overlying seat-earths and shales of the Upper Estuarine Series (1.2.3).

Although the geochemistry of the limestone is dependent to a large extent on the primary precipitates (ooliths, carbonate cements, pyrite and gypsum, etc.) and allochems (e.g. terrigenous material and shell debris), the precipitation of a variety of cement phases during diagenesis is also of significance. Emery (1986) identified ferroan and non-ferroan dolomite and calcite cements (1.2.4), which locally account for a large proportion of the rock.

Within the main body of the aquifer, lithologies range from carbonate-cemented oolites (90-95% $CaCO_3$) to lime muds with or without shell debris (70-90% $CaCO_3$), while bounding lithologies are

Figure 6.1

Molar plots of Mg, Sr, Fe and Mn against Ca. The samples from Bicker and Donington boreholes (denoted B and D, respectively), are all from the Lincolnshire Limestone. General trends are a function of the increasing calcium carbonate content of the limestones. Approximately half of the total calcium in samples B4 and D1 (Clipsham Member) occurs as sulphate, these samples do not therefore lie on the trend line. The arrow denotes a determination below the detection limit.



more argillaceous, containing approximately 10% SiO_2, up to about 70% gypsum and with a higher organic matter and clay mineral content. The overlying, predominantly clastic sequence of the Upper Estuarine Series is comparatively enriched in heavy metals, clay minerals etc. The contact between the two units is unconformable; thus, although the Upper Estuarine Series is essentially a confining unit, it is in places in hydraulic continuity with the Lincolnshire Limestone (Downing and Williams, 1969).

6.2.2 Minor cations associated with the carbonate phases

The molar concentrations of magnesium, iron, strontium and manganese are plotted against calcium in figure 6.1. Certain general trends are apparent: the Ca/Mg and Ca/Sr ratios remain fairly constant at 40-50 and 1500-2000 respectively; the fluctuations in the Ca/Mn ratio are greater, with a few determinations falling below the manganese detection limit, and the iron content tends to be inversely related to the calcium concentration, resulting in an increase in the Mg/Fe ratio. The exceptions to these general trends are samples B4 and D1 from the Clipsham Member (top of the formation) which are enriched in each cation, and B14, an oolite with clay lenses from the Greetwell Member (Lower Lincolnshire Limestone) which is enriched only in iron and manganese. In general the diagram demonstrates trends against increasing $CaCO_3$ content (or decreasing terrigenous input), however from table 5.1 and the estimation of gypsum in some samples, it is clear that in the more argillaceous samples only half of the calcium is bound up in calcite. If the actual $CaCO_3$ content was known accurately and used as the abscissa, these samples would probably lie closer to the trend lines. For example, sample B4, in the light of table 5.1, has of the order of only 3.7 moles of calcium incorporated in carbonate rather than sulphate phases, which would allow it to be plotted far

to the left of the graph.

Emery (1986) identified a variety of cement phases in the Lincolnshire Limestone, including high and low-magnesium calcite, ferroan calcite (25% of the rock by volume), non-ferroan calcite (5% of the total rock) and ferroan and non-ferroan dolomite. High-magnesium calcite was apparently precipitated in the marine environment, but was later nearly all stabilised to low-magnesium calcite. In the whole-rock samples from Bicker and Donington boreholes, $x < 0.02$ for the pure oolites and 0.023-0.033 for the argillaceous limestones, where:

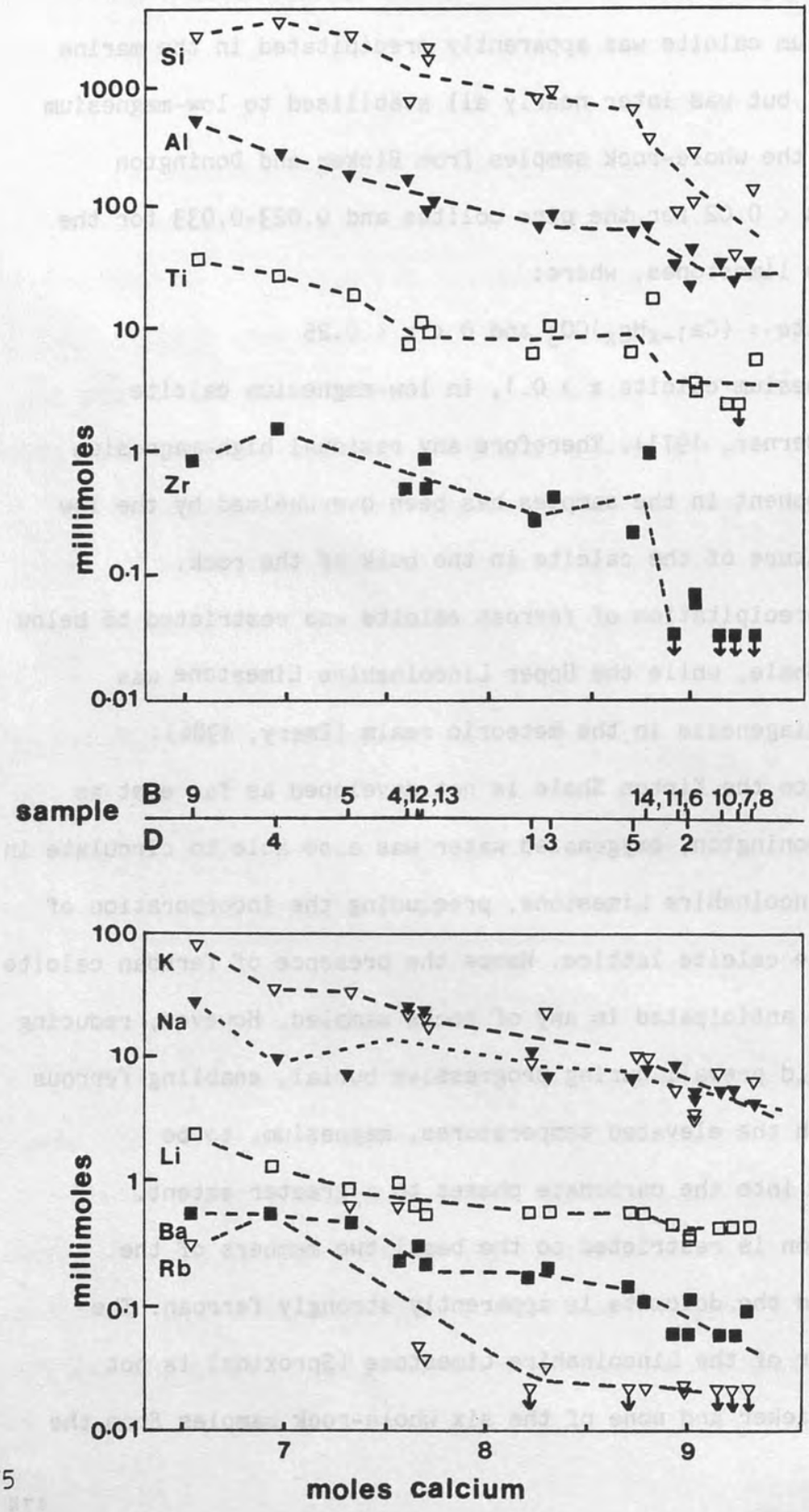
Calcite = $(Ca_{1-x}Mg_x)CO_3$ and $0 < x < 0.25$

In high-magnesium calcite $x > 0.1$, in low-magnesium calcite $x < 0.05$, (Berner, 1971). Therefore any residual high-magnesium calcite component in the samples has been overwhelmed by the low magnesium nature of the calcite in the bulk of the rock.

The precipitation of ferroan calcite was restricted to below the Kirton Shale, while the Upper Lincolnshire Limestone was undergoing diagenesis in the meteoric realm (Emery, 1986). However, since the Kirton Shale is not developed as far east as Bicker and Donington, oxygenated water was also able to circulate in the Lower Lincolnshire Limestone, precluding the incorporation of Fe^{2+} into the calcite lattice. Hence the presence of ferroan calcite would not be anticipated in any of rocks sampled. However, reducing conditions did prevail during progressive burial, enabling ferrous iron and with the elevated temperatures, magnesium, to be incorporated into the carbonate phases to a greater extent. Dolomitization is restricted to the basal two members of the formation and the dolomite is apparently strongly ferroan. The lowest member of the Lincolnshire Limestone (Sproxton) is not present at Bicker and none of the six whole-rock samples from the

Figure 6.2

Molar plots of nine elements associated with the non-carbonate phases in the limestone, against calcium. Samples are from Bicker (B) and Donington (D) boreholes. Determinations below the detection limit are indicated with an arrow.



Greetwell Member analysed, has a dolomite signature; the molar Ca/(Mg+Fe) ratios are all aproximately 50.

6.2.3 Minor elements associated with the non-carbonate phases

Molar abundances of several minor and trace elements are plotted in figure 6.2. The order of decreasing abundance is:

Si > Al > K > Ti > Na > Li > Zr > Ba > Rb

and each element is inversely related to the calcium concentration. Sample B14, an oolite containing clay lenses is more enriched in some elements (e.g titanium and zirconium) than other samples of the same calcium content. All the clay minerals identified by XRD (5.2.2) contain silicon and aluminium, however the major contributors of these elements are quartz and kaolinite which dominate the non-carbonate portion of every sample; illite and alkali feldspars are the main source of potassium, and the minor amounts of smectites provide calcium, sodium and iron (fig. 6.1). Biotite has also been identified (Emery, 1986) which contains all of the above plus titanium. Strontium (figure 6.1) is associated with detrital material - clays, potassium feldspars and micas - as well as the carbonate cement phases (Emery *et al.*, 1987).

In addition to the metals contained in the clay mineral structures, other ions are held at exchange sites or by surface adsorption (for example, rubidium). Group I and II metals are readily exchanged, most often for calcium, but also for other ions with a larger hydrated radius. Bivalent ions are exchanged in preference for univalent ions and the order of replaceability is:

Li < Na < K <Rb < Cs and Mg < Ca < Sr < Ba (Carroll, 1959).

In the Lincolnshire Limestone, the clay mineral group identified with the highest exchange capacity is the smectite group (80-150 meq/100g at pH7; Deer *et al.*, 1966), but is present only in small amounts. The considerable number of inter-layer potassium ions

in illite prevent the entry of other ions, therefore like kaolinite, its exchange sites are restricted to crystal edges. The exchange capacities of these two minerals are 10-40 and approximately 10 meq/100g respectively (Deer *et al.*, 1966).

The exchange capacity of organic matter is even higher than that of most clay mineral groups, capacities of 150-500 meq/100g have been quoted for organic material in soils (Carroll, 1959), therefore it has been suggested that organic matter in the Lincolnshire Limestone could be a site for ion-exchange. The organic content of the aquifer is not known in detail, although plant fragments and rootlets are clearly visible in hand specimen of argillaceous samples (for example, B3) and concentrations of organic material and clay minerals at solution seams/stylolites were reported by Emery (1986). Total organic carbon in oxidised and reduced Lincolnshire Limestone samples from close to outcrop was quantified by Edmunds (1973) (0.16% and 0.23% respectively) and the correlation between the reduced samples and higher values confirmed by Lawrence and Foster (1986). The organic carbon content of the argillaceous limestones at depth would be expected to be higher than these figures, possibly tending towards the average of 2% for sedimentary rocks (Krauskopf, 1979). However, considering the age of the aquifer, the time for rock-water contact etc. it is unlikely that the exchange capacities observed in soils would be appropriate for the mature organic matter of the Lincolnshire Limestone.

Hydrous iron and manganese oxides are ubiquitous as coatings around silicate grains and organic matter and as discrete grains of oxide material. The former may also contain other cations in addition to the iron and manganese (Drever, 1982; Carroll, 1959). An oolite containing clay lenses (B14, figure 6.1), therefore plots with higher iron and manganese concentrations than other samples of

comparable calcium content.

6.2.4 Trace elements

The concentrations of cobalt, copper, molybdenum and niobium are low in all the rock samples analysed, both in the pure oolites and the argillaceous limestones; however, chromium, nickel, scandium, vanadium and zirconium abundances increase with detrital/ non-carbonate content. Copper and cobalt are relatively depleted in samples from the Upper Estuarine Series.

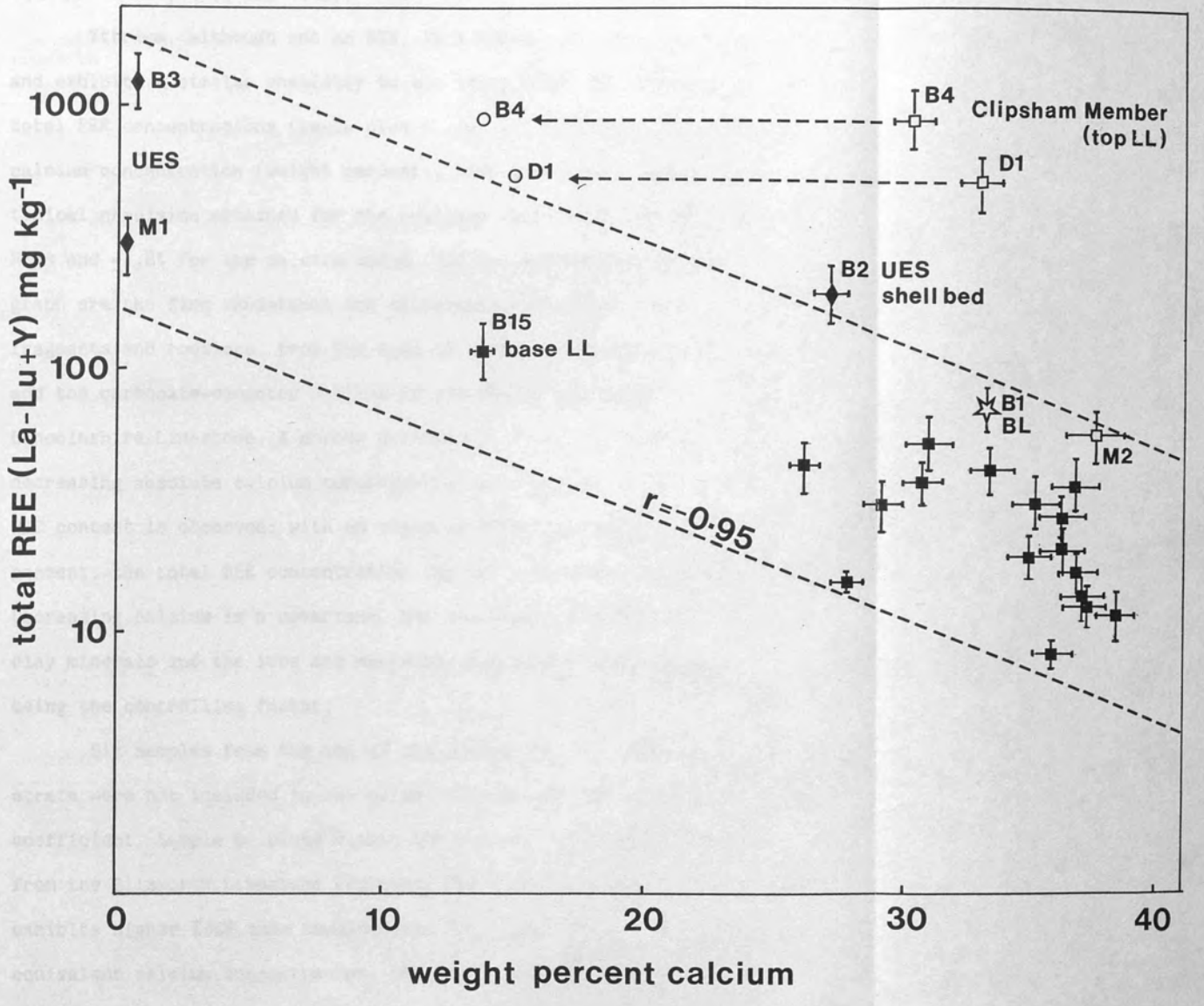
The mean concentrations (mg kg^{-1}) of the metals in eighteen Lincolnshire Limestone samples, in increasing order of abundance are: Zn (<5), Mo (<9), Sc (6), Cr (12), Co and Nb (16), V (28), Ni (43) and Zr (67). The role of the low geochemical abundance of these elements on the concentration of heavy metals in the Lincolnshire Limestone groundwaters is discussed in section 6.3.3.3.

6.2.5 Rare earth elements

The rare earth elements (La, Z=57 to Lu, Z=71) tend to occur in nature, as a group rather than in isolation, due to their electronic configuration. With increasing atomic number, electrons are added to the 4f orbital, well shielded by the completely-filled 5s, 5p and 6s orbitals; the 4f electrons are therefore not significantly involved in chemical reactions and the chemical behaviour of each element is similar. The only exceptions are La and Gd which have enhanced stability arising from the 4f sub-shells being empty and half-filled respectively (Clark, 1984; Henderson, 1984). The stable trivalent state and small but steady decrease in ionic radius with increasing atomic number (lanthanide contraction) are also due to the electronic configuration of the group. However, the occurrence of alternative oxidation states under natural conditions (for example, Ce^{4+} and Eu^{2+}) and the degree of fractionation, has led to the increasing importance of REE signatures in studies of petrogenesis

Figure 6.3

Total rare earth element (La-Lu, + Y) concentrations plotted against calcium, with error bars. Solid squares represent samples from the bulk of the Lincolnshire Limestone (LL); open squares - Clipsham Member; diamonds - Upper Estuarine Series (UES); the relative position of a single Blisworth Limestone sample (BL) is denoted with a star. Approximately half of the calcium in samples B4 and D1 (Clipsham Member) occurs as calcium sulphate; when the carbonate fraction only, is replotted (open circles), the points lie closer to the trend line.


B3
1000
B4
B4
Clipsham Member
(top LL)
UES
D1
D1
M1
B2 UES
shell bed
B15
base LL
100
B1
BL
M2
r = -0·95
10
total REE (La-Lu+Y) mg kg-1
0
10
20
30
40
weight percent calcium

(e.g. Haskin *et al.*, 1968); similarly the geochemistry of REEs in the marine environment has been the subject of considerable research (Goldberg, 1963; Martin *et al.*, 1976; Elderfield and Greaves, 1982; De Baar *et al.*, 1983 and 1985).

Yttrium, although not an REE, is a member of the group IIIB and exhibits a similar chemistry to the heavy REEs. In figure 6.3 total REE concentrations (La-Lu plus Y, mg kg^{-1}) are plotted against calcium concentration (weight percent), with error bars representing typical precision obtained for the analyses (4.6) of $\pm$ 11% for total REEs and $\pm$1.8% for the calcium value. The two end-members of the graph are the fine sandstones and siltstones containing plant fragments and rootlets, from the base of the Upper Estuarine Series, and the carbonate-cemented oolites of the Middle and Lower Lincolnshire Limestone. A strong correlation (r=-0.95) between decreasing absolute calcium concentration and increasing (relative) REE content is observed: with an increase in calcium of 10 weight percent, the total REE concentration (mg kg^{-1}) decreases by 61%. Decreasing calcium is a covariant, the depletion of organic matter, clay minerals and the iron and manganese hydroxides coating them being the controlling factor.

Six samples from the top of the aquifer or from overlying strata were not included in the calculation of the correlation coefficient. Sample B1 plots within the general trend lines but is from the Blisworth Limestone (formerly the Great Oolite); it exhibits higher ΣREE than samples from the Lincolnshire Limestone of equivalent calcium concentration. Samples B3 and M1 with high ΣREE content are typical of the Upper Estuarine Series, closest to the contact with the Lincolnshire Limestone; however the upper part of the Series contains shelly beds; the large Ostreas set in a shaley matrix raise the calcium concentration of B2 to 68%, while the ΣREE

Table 6.1

Summary table of the geochemistry of the Lincolnshire Limestone and associated strata.

stratigraphy/ lithology	sample no.	Ca by weight	ΣREE+Y mg kg^{-1}	La sample/ shale	shale normalised REE signature	relative enrichment in:
BLISWORTH LIMESTONE						
oolite	B1	33%	71	0.1	HREE depletion	Fe, P, Mn, Ni
UPPER ESTUARINE SERIES						
shell bed	B2	62%	198	1	Flat (Yb-Lu depletion)	Ca, Mg, K, Ti, Mn, Sr
siltstone	B3	<1% *1:5	1296	6	strong HREE depletion	Si, Al, Zr, (Sc, Mo, Nb)
LINCOLNSHIRE LIMESTONE						
<u>argillaceous limestones:</u>						
Clipsham Member (shell bed)	M2	38%	59	0.2	slight MREE enrichment	Ca, Mg, Sr
(clastic/ gypsiferous)	B14, D1	30-33% *1:2	517-930	5	strong M/HREE depletion	mod: REEs + Y
base Lincs. Limestone	B15	14%	119	5	flat	strong: K,P, Mg, Na, Mn, Fe, Sr, Ti
	B12-14, B5, B9 D3-4	26-35% *1:0.8	16-84	0.1-0.3	flat	↑ ↓
<u>oolitic limestones:</u>						
	B6-8, B10-11, D2, D5	35-37% (90-95% $CaCO_3$)	9-28	<0.1	flat	Ca

*The ratio of calcium present as carbonate or gypsum (CO_3:SO_4) is indicated where known

remains high at 198 mg kg^{-1}. The Clipsham Member (B4, D1 and M2), at the very top of the Lincolnshire Limestone is a very thin unit at these sites, and exhibits a very different lithology and chemistry to other argillaceous limestones in the formation, more akin to that of the Upper Estuarine Series. Sample M2 is from the base of the Clipsham Member (1 m below the contact), it is a hard limestone, incorporating little clay, but significant shell debris. The sample has a higher REE content than the pure limestones, but plots close to the samples from the bulk of the aquifer and was therefore included in the calculation. Samples B4 and D1 are hard granular samples containing clay lenses of 1-2 mm thickness, from 20-30 cm below the contact with the Upper Estuarine Series. Gypsum accounts for almost half of the calcium in these samples, therefore when this portion is disregarded the ΣREE concentrations plot closer to the trend line, however they still contain anomalously high amounts of the rare earths and were not included in the calculation of the correlation coefficient.

6.2.6 Summary

The geochemistry of samples from the Lincolnshire Limestone and overlying strata at Bicker and Donington boreholes are summarised in table 6.1. The samples are tabulated on the basis of calcium and rare earth element content, REE signature and relative enrichment of major cations and trace metals.

6.3 GROUNDWATERS

6.3.1 Spatial hydrochemical trends

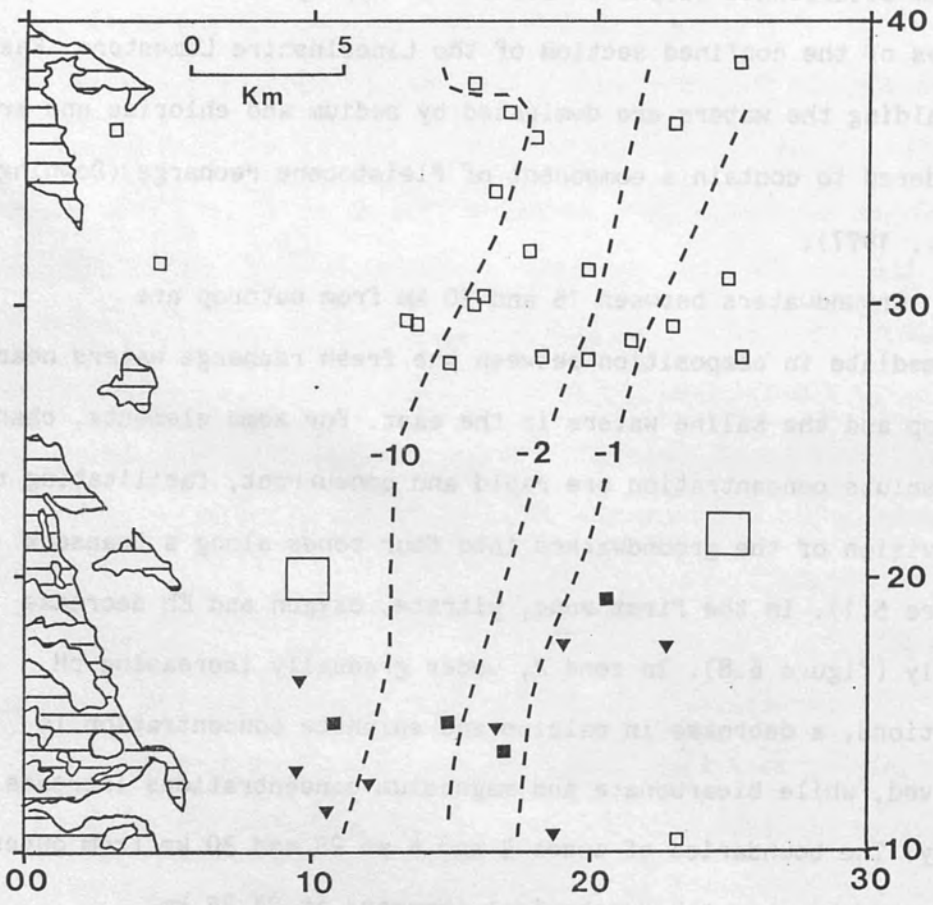
The two end-members of the groundwater system in the confined section of the Lincolnshire Limestone aquifer are calcium-bicarbonate-sulphate dominated recharge waters in the west and saline waters in the east. The aquifer is recharged at outcrop 15 km west of the most westerly site of this study. Atmospheric inputs

include sodium, chloride and tritium; runoff from agricultural land adds significant quantities of calcium, sulphate and nitrate during periods of low stream flow. For the first 10 km downdip from outcrop, carbonate equilibria resulting from the interaction of the recharge waters and limestone are dominant controls on the hydrochemistry of the aquifer; calcium, bicarbonate and pH increase, while chloride and nitrate concentrations decrease, yielding the calcium-bicarbonate-sulphate waters that typify the most westerly samples of the confined section of the Lincolnshire Limestone. East of Spalding the waters are dominated by sodium and chloride and are considered to contain a component of Pleistocene recharge (Downing *et al.*, 1977).

Groundwaters between 15 and 30 km from outcrop are intermediate in composition between the fresh recharge waters near outcrop and the saline waters in the east. For some elements, changes in absolute concentration are rapid and concurrent, facilitating the subdivision of the groundwaters into four zones along a transect (figure 5.1). In the first zone, nitrate, oxygen and Eh decrease rapidly (figure 6.8). In zone 2, under gradually increasing pH conditions, a decrease in calcium and sulphate concentration is observed, while bicarbonate and magnesium concentrations increase slowly. The boundaries of zones 3 and 4 at 25 and 30 km from outcrop are marked by abrupt hydrochemical changes: at 24-25 km, conductivity, sodium, lithium, chloride, bromide and iodine commence a rapid increase in concentration; bicarbonate and pH also rise more rapidly; calcium and sulphate decrease slowly; magnesium, strontium, barium and silicon decrease to at or below their concentration levels in zone 2. At 29-30 km, the increase in the other alkali metals commences and the rise in halide concentrations (with the exception of fluoride) accelerates, chloride levels exceeding

Figure 6.4

$\delta^{13}C$ values (permil) for groundwaters from the southern Lincolnshire Limestone. Legend as in figure 5.1. Source of data: open squares - Bishop (1988); solid squares - Downing *et al.* (1977); solid triangles - Lawrence *et al.* (1976)



200 mg l^{-1}, the EEC maximum limit for public potable supplies, (Cook and Miles, 1980). Calcium, sulphate and magnesium increase again; bicarbonate concentrations and pH level off.

6.3.1.1 Carbonate equilibria

In the soil zone at and near outcrop, up to 20-30 mg l^{-1} dissolved carbon dioxide (Lawrence *et al.*, 1976) is taken up by infiltrating rainwater. Carbonic acid then dissociates and carbonates go into solution as bicarbonates causing a gradual rise in pH according to the following reactions (Downing and Williams, 1969):

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^- \qquad (pH > 8.2)$$

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$$

Saturation with respect to calcium carbonate is quickly attained in the north and south of the area and the groundwaters remain saturated or slightly undersaturated until 28-29 km from outcrop.

Groundwater $\delta^{13}C$ values from Lawrence *et al.* (1976), Downing *et al.* (1977), and Bishop (1988) are presented in figure 6.4. The data become progressively less negative in the direction of groundwater flow, indicating that calcium carbonate is being continuously dissolved and reprecipitated as the groundwater migrates downdip (Smith *et al.*, 1975). The initial $\delta^{13}C$ ratio is controlled by the reaction:

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca(HCO_3)_2$$

where $\delta^{13}C$ values are (approximately): +2.35 permil ($CaCO_3$); -26 permil (CO_2) and -12 permil (HCO_3^-). Values of -13 to -11 permil at 10 km from outcrop indicate that half of the dissolved carbonate species are derived from soil-CO_2 (Downing *et al.*, 1977); after dissolving carbonate in the limestone and reprecipitating calcite for a distance of 30 km, the signature of the groundwater approaches

Figure 6.5

Plot of saturation indices for calcite against dolomite. Open squares represent groundwaters from zone 1; solid triangles - zone 2; open circles - zone 3; solid squares - zone 4. The trend from under- to oversaturation proceeds with the passage of groundwater downdip.

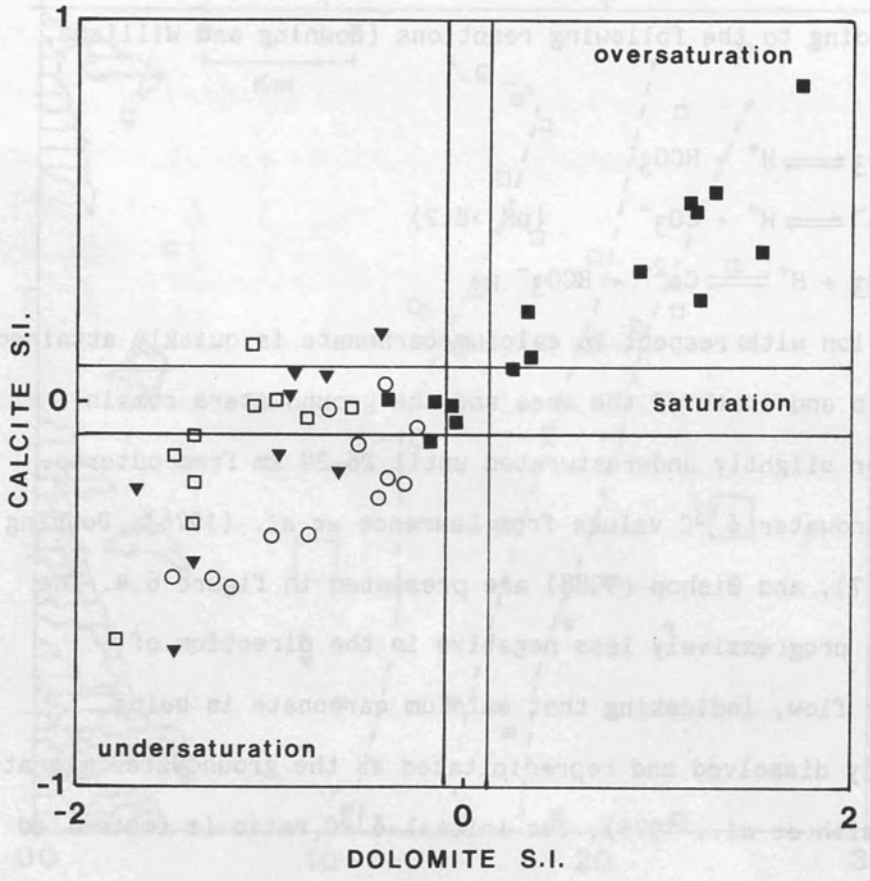
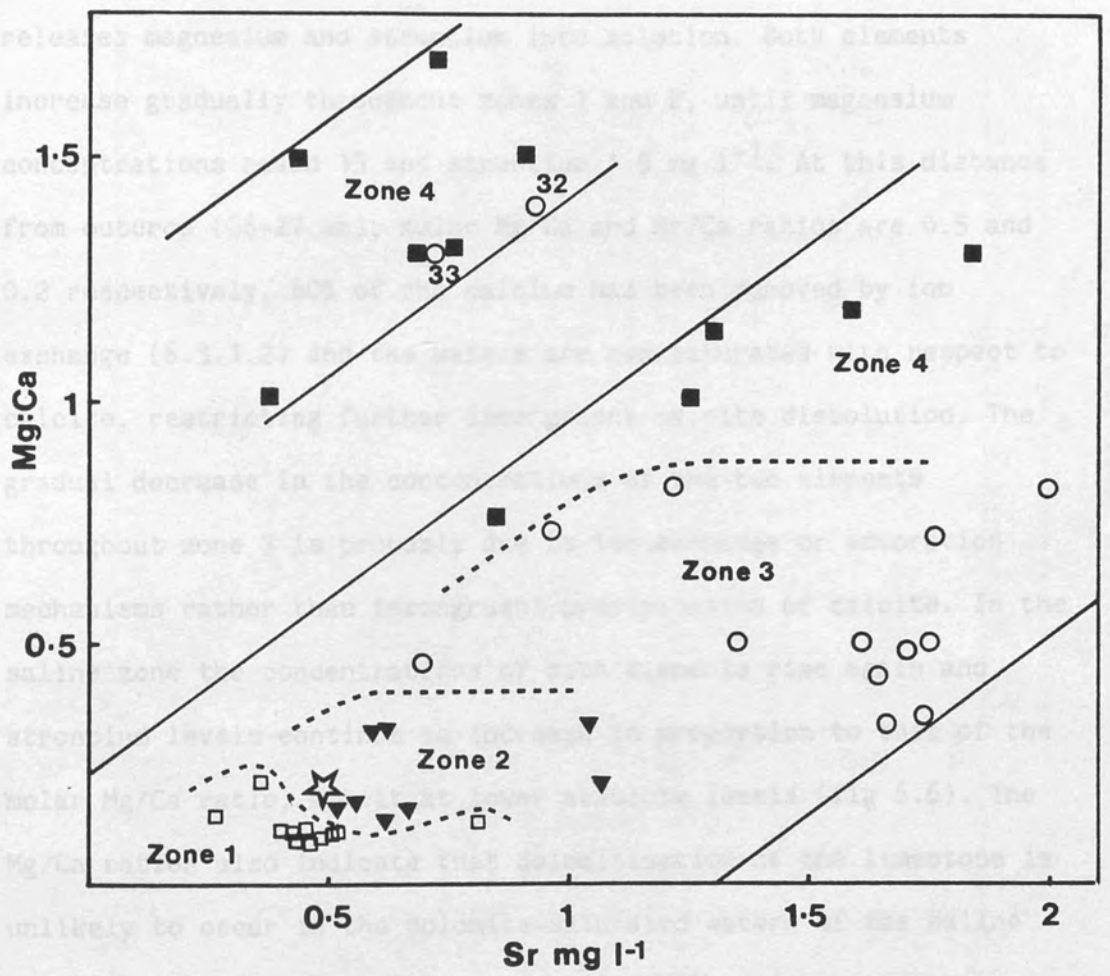


Figure 6.6

Molar Mg/Ca ratios plotted against strontium. Although the major ion chemistry of samples 32 and 33 is similar to that of zone 4 groundwaters, the chlorinity does not exceed 200 mg l^{-1}, and therefore they are included in zone 3 (see figure 6.8). The values for the most saline sample (Moulton West Fen, denoted by a star) have been divided by 10.



that of the aquifer matrix, with the lightest value of +0.3 permil at Crowland Bridge.

The spatial trends of magnesium and strontium are very similar, and the ratios Sr/Ca, Sr/Mg and Mg/Ca all increase eastwards, although the waters become increasingly oversaturated with respect to calcite, dolomite and strontianite with distance downdip (figures 6.5 and 6.6). While the calcite is being continuously dissolved and reprecipitated, $\overset{net}{\swarrow}$ incongruent dissolution releases magnesium and strontium into solution. Both elements increase gradually throughout zones 1 and 2, until magnesium concentrations reach 15 and strontium 1.5 mg l^{-1}. At this distance from outcrop (26-27 km), molar Mg/Ca and Sr/Ca ratios are 0.5 and 0.2 respectively, 60% of the calcium has been removed by ion exchange (6.3.1.2) and the waters are oversaturated with respect to calcite, restricting further incongruent calcite dissolution. The gradual decrease in the concentrations of the two elements throughout zone 3 is probably due to ion exchange or adsorption mechanisms rather than incongruent precipitation of calcite. In the saline zone the concentrations of both elements rise again and strontium levels continue to increase in proportion to that of the molar Mg/Ca ratio, albeit at lower absolute levels (fig 6.6). The Mg/Ca ratios also indicate that dolomitization of the limestone is unlikely to occur in the dolomite-saturated waters of the saline zone, as a concomitant rise in both ions is apparent (the Mg/Ca ratio ranges from 1-1.5).

6.3.1.2 Ion exchange

The processes of ion exchange and mixing with saline water are clearly illustrated in figure 6.7, in which sodium concentrations are plotted against calcium. Initially, calcium levels decrease along line A, due to calcite precipitation, while

Figure 6.7

Plot of calcium against sodium concentrations. Open squares - groundwaters from zone 1; solid triangles - zone 2; open circles - zone 3; solid squares - zone 4. Calcium concentrations decrease along line A due to calcite precipitation, and between lines A and B due to ion exchange for sodium; lines A and B are the boundaries of zones 1/2 and 2/3, respectively (see figure 6.8).

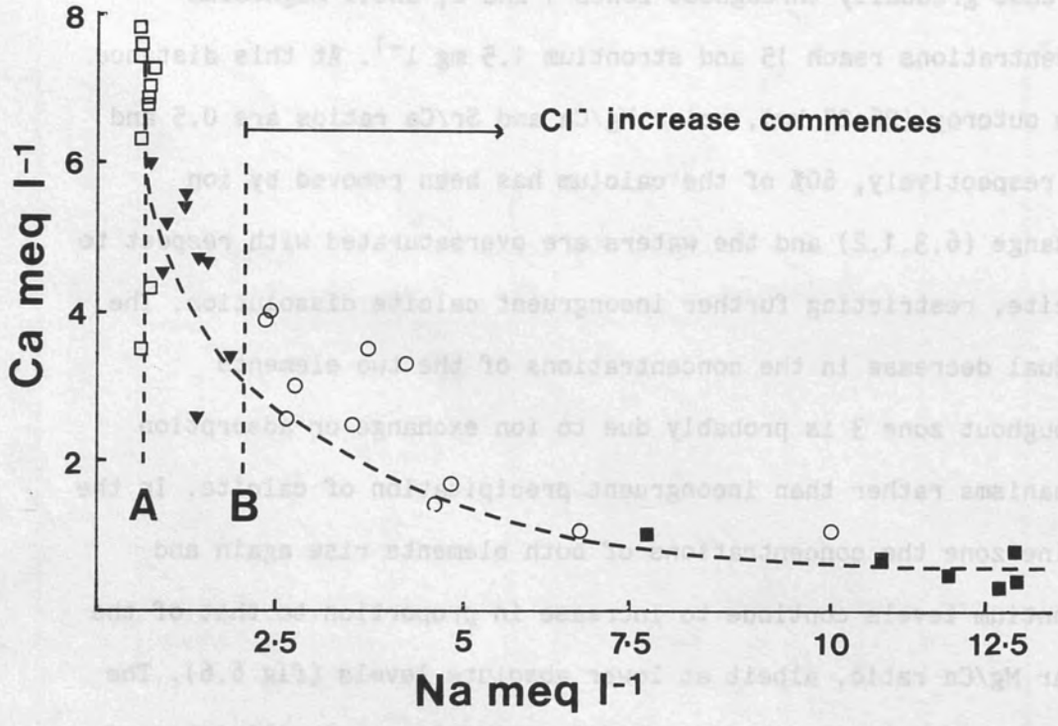
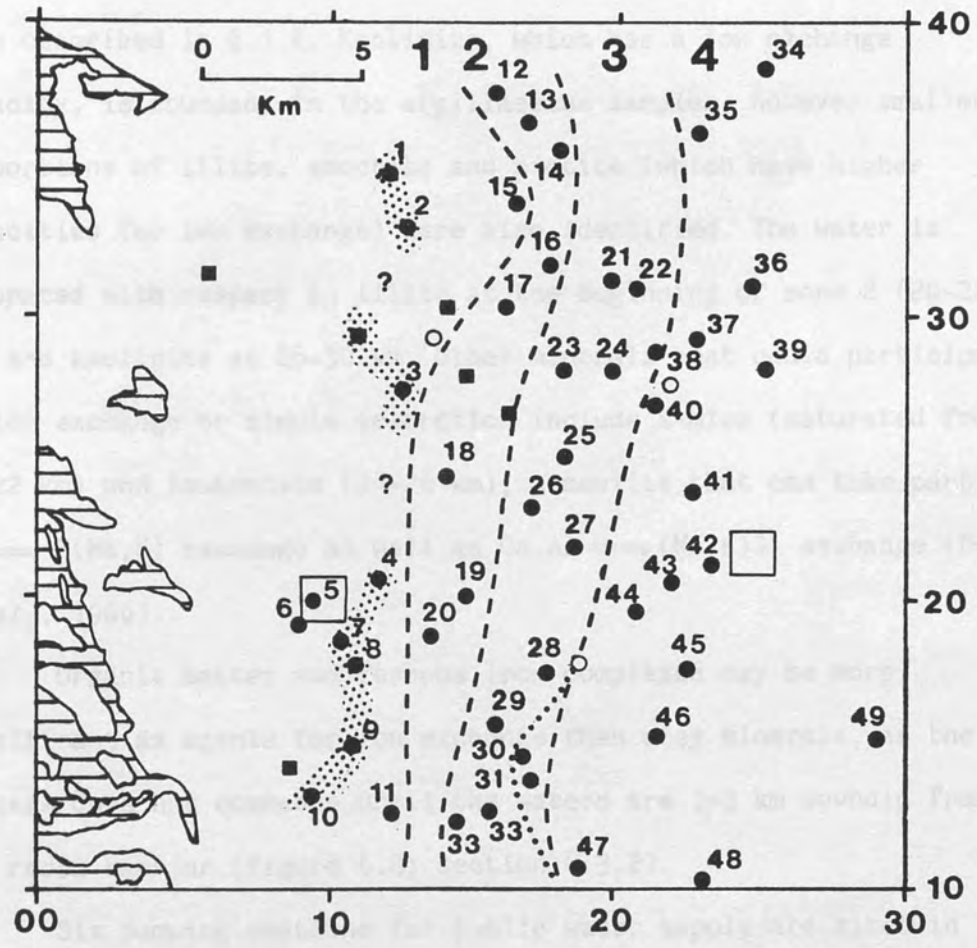


Figure 6.8

Lincolnshire Limestone groundwater zones used in this study; individual sites are identified by sample numbers. The boundaries of zones 1/2 and 2/3 are delineated by lines A and B in figure 6.7, zone 2 being the zone of Ca-Na ion exchange. The boundary of zone 3/4 is the limit of potable water (200 mg l^{-1} isochlor) and also the boundary of Na-HCO_3 and Na-HCO_3-Cl type waters, except in the extreme south where the latter is indicated by a dotted line. The location of the "redox barrier" (6.2.2) is denoted by the stippled area.



sodium concentrations remain constant at 0.5 meq l^{-1}. The calcium decrease continues and the Na/Cl ratio rises from 1.5 to 3.5, due to the release of sodium ions from cation exchange sites and their replacement by calcium. By the beginning of zone 3, (line B), sodium levels have risen to 2 meq l^{-1} and chloride commences its proportional increase as mixing with saline water becomes significant.

The clay mineral content of the Lincolnshire Limestone has been described in 6.1.4. Kaolinite, which has a low exchange capacity, is abundant in the argillaceous samples, however smaller proportions of illite, smectite and biotite (which have higher capacities for ion exchange) were also identified. The water is saturated with respect to illite at the beginning of zone 2 (20-22 km) and kaolinite at 26-30 km. Other minerals that could participate in ion exchange or simple adsorption include K-mica (saturated from 20-22 km) and laumontite (24-26 km), a zeolite that can take part in $Ca \rightleftharpoons 2(Na,K)$ exchange as well as $Ca,Al \rightleftharpoons (Na,K)Si$ exchange (Deer *et al.*, 1966).

Organic matter and ferrous iron complexes may be more significant as agents for ion exchange than clay minerals, as the process does not commence until the waters are 1-3 km downdip from the redox barrier (figure 6.8; section 6.3.2).

Six pumping stations for public water supply are sited in zones 1 and 2. The suitability of the latter was first identified by Lamont (1958): ion exchange within the zone has brought about the natural softening of the carbonate-buffered recharge waters of zone 1, to the sodium-calcium-bicarbonate type waters of zone 3; and fluoride concentrations are at ideal levels for the prevention of dental caries.

6.3.1.3 Mixing between saline and recharge waters

In figure 6.7, the initial rise in chloride levels, proportional to that of sodium is identified by line B. Five km downdip, sodium concentrations have risen to 7 meq l^{-1}, and the chloride exceeds the maximum level for potable water (5.6 meq l^{-1}, 200 mg l^{-1}). Line B and the 200 mg l^{-1} isochlor denote the western boundaries of zones 3 and 4 at 25 and 30 km from outcrop respectively. These boundaries also mark rapid increases in the concentrations of lithium, bromide and iodine (zone 3), and sulphate, the alkali earths, and remaining alkali elements (zone 4). The four zones used in the discussion of major and minor element chemistry are mapped in figure 6.8.

There are no public supply boreholes in zone 3, since the advised limit for fluoride (1.5 mg l^{-1}) is frequently exceeded. However, abstraction rates further updip are high enough to locally lower piezometric levels and reverse the hydraulic gradient. With the supply of recent recharge via fissures diminished, the saline interstitial component of the groundwater increases; therefore by 30 km from outcrop where east-west flow is neglible, the major ion chemistry of the groundwaters is dominated by sodium, bicarbonate and chloride, becoming sodium-chloride type within a further two or three km.

Lawrence *et al.* (1976) demonstrated clear straight-line mixing relationships between recharge and saline waters, across an "interface zone", attributing the accelerated increase in sodium and decrease in calcium at the beginning of this zone to base exchange. Zone 2 of this study therefore approximates with the eastern section of their "interface zone", zone 3, with the rest.

Chloride, bromide and total iodine rise concurrently at the beginning of zone 3 and continue to rise rapidly in the saline zone.

A fairly constant Cl/Br ratio of 500-600 is maintained across the area, while the Cl/I ratio decreases rapidly from 3000 to 500. Both these and the Cl/F ratio are at their minimum in zone 3. The increase in fluoride concentrations would appear to be checked by the approach of saturation with fluorite; however, the initial liberation of both fluoride and iodine is probably controlled by redox processes (6.3.2). The bromide increase is the result of mixing, as it exhibits a stronger correlation with distance from outcrop than with Eh.

In the saline zone, the levels of group I and II metals and sulphate increase rapidly with distance from outcrop. Maximum concentrations of boron, phosphorus, barium and strontium, in addition to the halides and alkali metals are observed in the groundwaters from the sites furthest from outcrop. This phenomenon is probably due to a combination of the residence time of the pore-waters in the aquifer and membrane-filtration effects (6.4).

A gradual increase in the percentage of sodium and chloride ions with distance from outcrop would be expected to coincide with the eastward salinity increase; the trend is observed until 31 km, however, Moulton West Fen (site 49), the most easterly sample, is anomalous in this respect. While chloride concentrations increase and bicarbonate and sulphate decrease as a percentage of total anions, as expected, the percentage of sodium and potassium ions decrease and calcium and magnesium levels increase. In addition, instead of Eh decreasing further and the pH rising, the reverse is true. Increasing undersaturation with respect to the major sulphate minerals suggests that dissolution of gypsum and barite etc. accelerates at this distance downdip, causing the observed increase in absolute concentrations of calcium, magnesium, strontium, barium and sulphate, which are large enough to counteract the increase in

sodium concentration, and thus reduce its percentage of total cations. No samples could be taken between Crowland Bridge (site 48), at 31.6 km from outcrop and Moulton West Fen (36.8 km) to confirm the trend, however.

The major ion chemistry of the interstitial waters and the source of the saline water is considered in 6.4.

6.3.2 Hydrochemical trends related to redox processes

Redox processes have been shown to have a significant control on the mobilities of transition metals such as iron and manganese and species taking part in the carbon, nitrogen, oxygen and sulphur cycles (Back and Barnes, 1965; Langmuir, 1971; Edmunds, 1973; Champ *et al.*, 1979 etc.).

The reduction-oxidation potential of the water is represented by Eh measured with a platinum electrode. However, since most natural waters have very low concentrations of species that take part in redox reactions and exchange rates of electrons both in solution and at the electrode are extremely slow, the measured Eh seldom reflects redox equilibria through the Nernst equation. A mixture of redox potentials rather than an equilibrium potential is often obtained. This is particularly likely in waters, such as the Lincolnshire Limestone, which have dissolved iron and manganese concentrations below 10^{-5} or 10^{-6} M (Lindberg and Runnels, 1984; Champ *et al.*, 1979). However, since the direct measurement of the potential of each redox couple in solution is impractical, Eh as a field parameter is still of considerable use if interpreted qualitatively or semi-quantitatively (Edmunds, 1976).

Champ *et al.* (1979) demonstrated that, in a confined aquifer containing some solid phase Mn(IV) and Fe(III) minerals and excess DOC, oxidised species would be reduced in the following sequence: O_2, NO_3, Mn(IV), Fe(III), SO_4, HCO_3 and N_2. Reduction zones at

Table 6.2

REDOX REACTIONS IN A CLOSED GROUNDWATER SYSTEM

Reaction	Equation	$G^o(w)$ (kcal)
Aerobic respiration	$CH_2O + O_2 = CO_2 + H_2O$	-120.0
Denitrification	$CH_2O + (4/5)NO_3^- + (4/5)H^+ = CO_2 + (2/5)N_2 + (7/5)H_2O$	-113.9
Mn(IV) reduction	$CH_2O + 2MnO_2 + 4H^+ = 2Mn^{2+} + 3H_2O + CO_2$	-81.3
Fe (III) reduction	$CH_2O + 8H^+ + 4\,Fe(OH)_3 = 4Fe^{2+} + 11H_2O + CO_2$	-27.7
Sulfate reduction	$CH_2O + (1/2)SO_4^{2-} + (1/2)H^+ = (1/2)HS^- + H_2O + CO_2$	-25.0
Methane fermentation	$CH_2O + (1/2)CO_2 = (1/2)CH_4 + CO_2$	-22.2
Nitrogen fixation	$CH_2O + H_2O + (2/3)N_2 + (4/3)H^+ = (4/3)NH_4^+ + CO_2$	-19.2

(after Champ *et al.*, 1979; modified after Stumm and Morgan, 1970)

various Eh values were identified and the most significant reactions in the closed system are indicated in table 6.2.

A "redox barrier" was observed by Edmunds (1973) and defined as a drop of 300 mV in the Eh values of the groundwaters, coinciding with a sharp decrease in dissolved oxygen and nitrate levels. The location of the feature at 17-18 km from outcrop has remained fairly stationary since 1969 as discussed in 6.3.4.3. The position of the redox barrier is indicated in figure 6.8.

The concentrations of fluoride, iodine, nitrate (as nitrogen), dissolved oxygen and reduced species measured as total iron, total manganese and sulphide, are plotted against Eh from +400 to -400 mV (figure 6.9). Samples collected by BGS in 1982-83 have been included, since they demonstrate redox conditions further upgradient in the aquifer, i.e. at higher Eh values. The general pattern observed, at approximate Eh values, is:

1. O_2 and NO_3 concentrations decrease to detection limit values at +250 to +200 mV
2. Mn > 1 $\mu g\ l^{-1}$ at +350 mV
3. Fe and S > 1 $\mu g\ l^{-1}$ at +170 mV

6.3.2.1 Oxygen

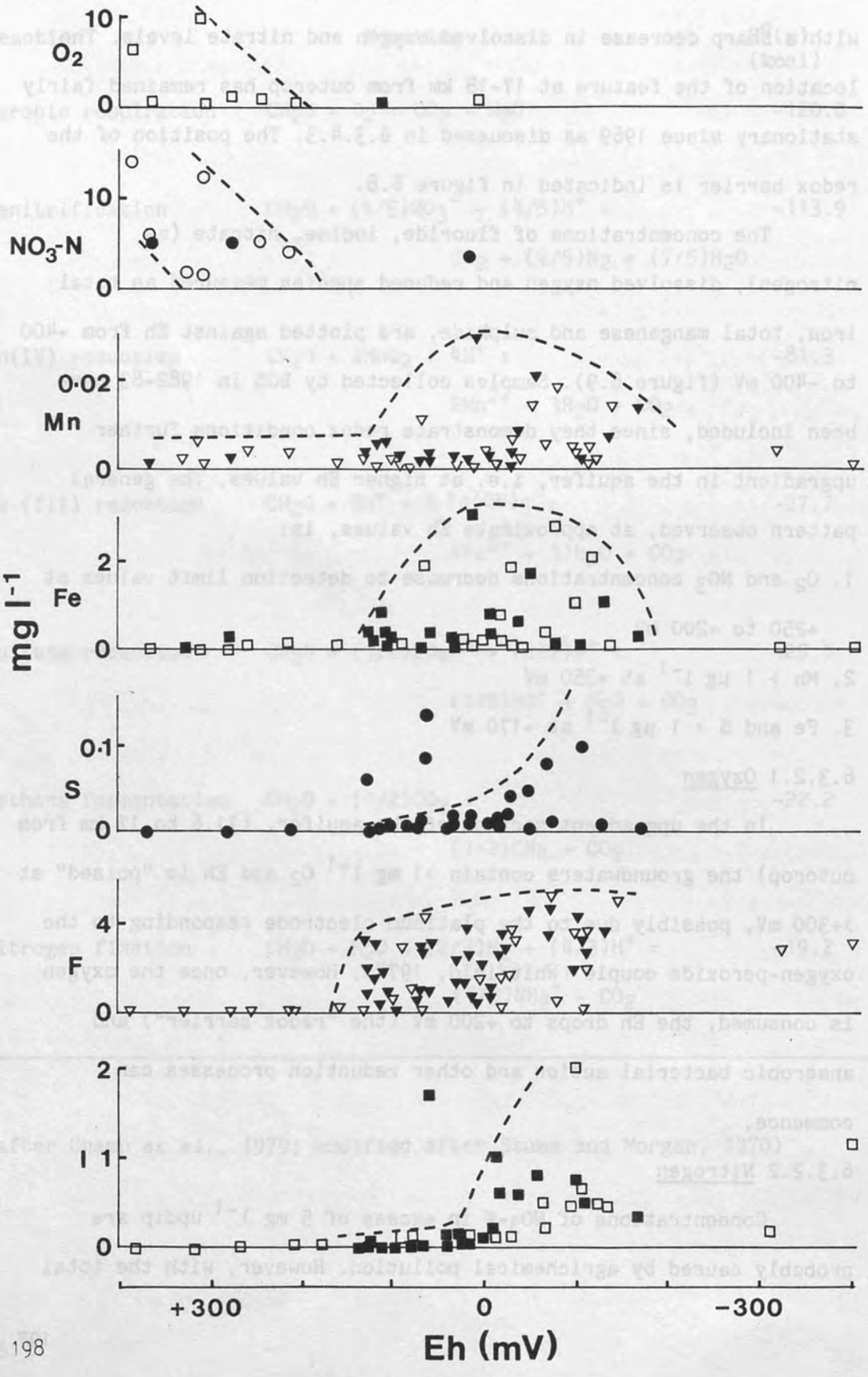
In the upgradient section of the aquifer, (11.6 to 17 km from outcrop) the groundwaters contain >1 mg l^{-1} O_2 and Eh is "poised" at >+300 mV, possibly due to the platinum electrode responding to the oxygen-peroxide couple (Whitfield, 1974). However, once the oxygen is consumed, the Eh drops to +200 mV (the "redox barrier") and anaerobic bacterial action and other reduction processes can commence.

6.3.2.2 Nitrogen

Concentrations of NO_3-N in excess of 5 mg l^{-1} updip are probably caused by agrichemical pollution. However, with the total

Figure 6.9

Concentrations of oxygen, nitrate (as nitrogen), manganese, iron, sulphide, fluoride and iodine in mg l^{-1} plotted against redox potential (Eh). Open and solid symbols represent 1983 (BGS) and 1984-85 determinations respectively.



consumption of dissolved oxygen and the drop of Eh to +200 mV, the nitrate values also decrease to detection limit levels i.e < 0.4 mg l^{-1} N.

In the absence of oxygen, anaerobic denitrifying bacteria reduce nitrate according to the reaction:

$$CH_2O + 4/5NO_3^- + 4/5\ H^+ \xrightarrow{\text{bacteria}} CO_2 + 2/5N_2 + 7/5H_2O$$

Lawrence *et al.* (1986) identified potential denitrifying bacteria in oxidised limestone close to fissures and adequate organic matter for the bacteria in the residual lenses of reduced limestone. Nitrates were not detected in interstitial waters from the aquifer at depth, but thermonuclear tritium, indicative of post-1953 recharge, was identified. This absence of nitrates is thus more likely to be due to bacterial denitrification rather than to the lack of a recent nitrate-bearing recharge component in the deeper waters.

With the increased usage of fertilisers on the outcrop of the Lincolnshire Limestone, the infiltration of contaminated surface water from "losing streams" due to overabstraction is a potential problem. However, although a slight increase in nitrates has been detected in groundwaters from the unconfined zone, encroachment beyond the redox barrier has not been observed (6.3.4). Edmunds and Walton (1983) inferred that the nitrate-reducing capacity of the aquifer is at present large enough to cope with the increased nitrate input.

6.3.2.3 Iron

The mean concentration of total iron in eighteen limestones is only 0.5% and total dissolved iron values in the uncontaminated groundwaters range from <0.5 to 863 µg l^{-1}, with the mean at 194 µg l^{-1}. Under the prevailing Eh/pH conditions and at equilibrium, iron concentrations of the order of 5.6 to 56 µg l^{-1} would be anticipated (Hem, 1970), that is, 1-2 orders of magnitude below

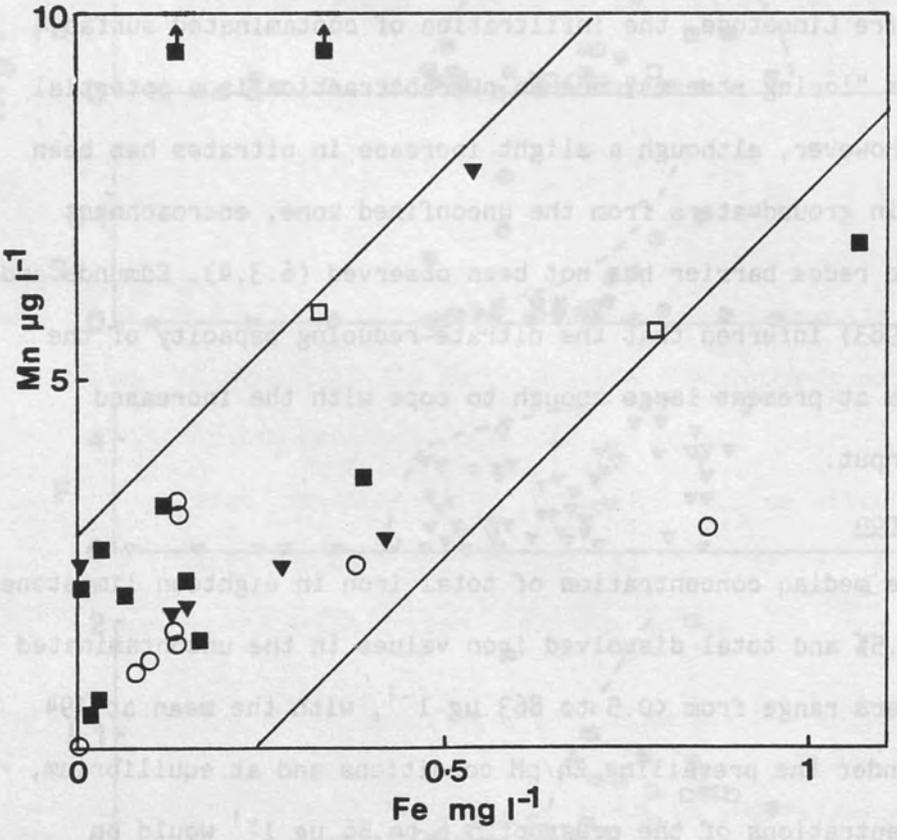
Table 6.3

Determinations of total manganese, dissolved oxygen and redox potential in groundwaters from zone 1. Determinations by BGS (1982/83) are indicated by an asterisk.

	$Mn_{(T)}$	O_2	Eh
	$\mu g\ l^{-1}$	$mg\ l^{-1}$	mV
*	<0.2	6.7	+411
*	<0.2	1.7	+350
	<0.2	0.5	+330
	1.9	1.0	+301
*	4.2	1.0	+270
*	2.9	0.5	+390
*	4	0.5	+236
*	1.3	<0.2	+31
	14.3	<0.2	+300

Figure 6.10

Covariance of manganese and iron concentrations in the Lincolnshire Limestone groundwaters.



those reported. The effect of contamination, geochemical abundance and adsorption etc. are discussed in 6.3.3, however, the initial release of iron into solution is clearly controlled by redox processes. As aerated waters migrate downdip into the confined zone, low iron concentrations are maintained by the precipitation of ferric hydroxide. Once Eh values drop below +150 mV (figure 5.9) reduction to ferrous iron proceeds according to the reaction:

$$CH_2O + 8H^+ + 4Fe(OH)_3 \rightleftharpoons 4Fe^{2+} + 11H_2O + CO_2$$

(Edmunds *et al.*, 1984) and concentrations in excess of 100 µg l^{-1} appear in the groundwaters.

Saturation indices for the groundwaters (figure 5.11) indicate that saturation with respect to maghemite (Fe_2O_3) is coincident with the redox barrier, however, saturation with respect to amorphous $Fe(OH)_3$ is delayed for a further 5-10 km downdip. In zones 2 and 3 the groundwaters also attain saturation with respect to mackinawite (FeS) and siderite ($FeCO_3$) while saturation indices are close to zero across the whole of the confined zone for amorphous FeS precipitate. The precipitation of amorphous sulphide is therefore likely to limit iron concentrations downdip, once the redox potential drops to between -150 and -300 mV.

6.3.2.4 Manganese

The mean manganese concentration for uncontaminated waters (6.3.3) is 3.1 µg l^{-1}. Low levels of manganese are maintained by the precipitation of MnO_2 until dissolved oxygen concentrations decrease to <1 mg l^{-1} (table 6.3), when reduction occurs according to the reaction:

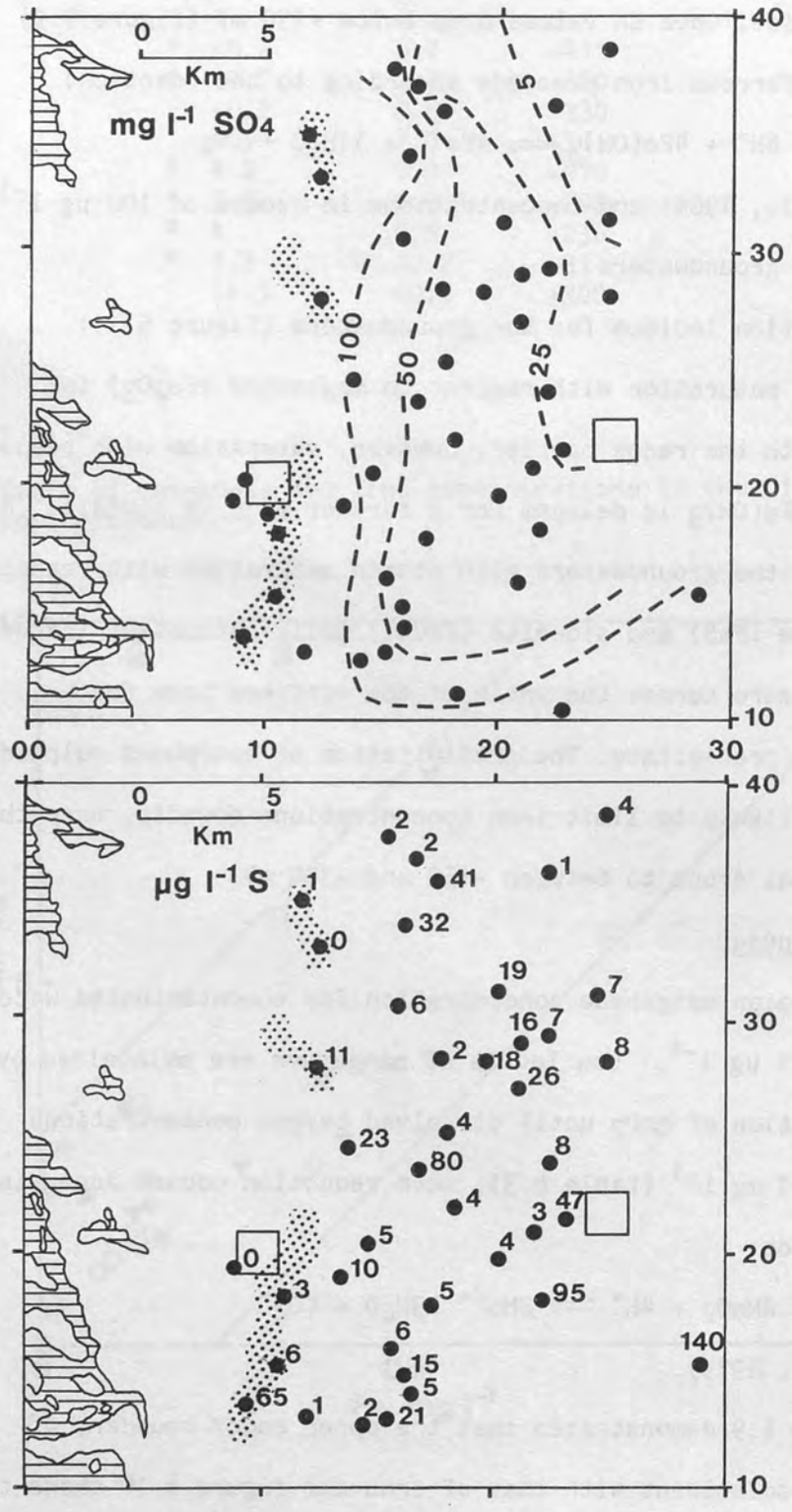
$$CH_2O + 2MnO_2 + 4H^+ \rightleftharpoons 2Mn^{2+} + 3H_2O + CO_2$$

(Champ *et al.*, 1979).

Figure 6.9 demonstrates that the upper redox boundary of manganese is coincident with that of iron and figure 6.10 shows the

Figure 6.11

Sulphur species in the groundwaters of the Lincolnshire Limestone. In the upper diagram sulphate concentrations (mg l^{-1}) are contoured; in the lower diagram, dissolved sulphide determinations (µg l^{-1}) are presented by the appropriate sample site. The stippled zone represents the redox barrier.



significant correlation of manganese and iron in groundwaters throughout the unconfined zone. It has been suggested therefore, that MnO_2 is released on the reduction of $Fe(O.OH)_3$ (Edmunds *et al.*, 1984).

6.3.2.5 Sulphur

The high sulphate levels in zone 1 (140-150 mg l^{-1}) are due to gypsum dissolution, pyrite oxidation and agrichemical contamination and decrease to approximately 25 mg l^{-1} around Spalding and to 1 mg l^{-1} in the north-east of the area (figure 6.11).

In general, dissolved sulphide was only determined in groundwaters with Eh values below +150 mV, although an anomalously high concentration (65 µg l^{-1}) was obtained at site 11. Dissolved sulphide at concentrations in excess of 10 µg l^{-1} are observed at a few sites 3-4 km downdip of the redox barrier, however the highest concentrations tend to be from samples south and east of Spalding (figure 6.11); the maximum dissolved sulphide concentration (140 µg l^{-1} S) was recorded at Moulton West Fen, the furthest site from outcrop. The data are of the same order of magnitude as determinations obtained in 1969 (Edmunds, 1973). In 1982 sulphide could only be detected by smell in samples at least 2 km east of the redox barrier, in 1985 H_2S could only be detected by smell in samples much further downdip.

The decrease in sulphate levels and increase in dissolved sulphide concentrations with distance from outcrop, has often been assumed to be wholly due to bacterial activity: the increasing undersaturation with respect to gypsum, anhydrite and barite (figure 5.11) precludes the involvement of sulphate precipitation in this phenomenon and sulphate-reducing bacteria were identified in limestone core from sites in zones 2 and 3 by Downing *et al.* (1977).

One or more of the following equations could be important in this process (Edmunds *et al*, 1984):

$$Fe_S + 8H_2O \rightleftharpoons 2SO_4^{2-} + Fe^{2+} + 7H^{2+}$$

$$CH_2O + SO_4^{2-} + H^+ \rightleftharpoons HS^- + 2CO_2 + 2H_2O$$

$$Fe^{2+} + HS^- \rightleftharpoons FeS_{ppt} + H^+$$

Additional sulphate for the reaction could be provided by the oxidation of fine grained pyrite in the grey limestone of the fissure walls by aerated water, and organic matter in the limestone itself could serve as a carbon source for the bacteria (Lawrence *et al*., 1976). However, carbon isotope data provide no evidence for the involvement of carbonaceous matter in the reaction. The bicarbonate produced from such a reaction would be expected to have a more negative $\delta^{13}C$ signature; in fact the values become far less negative in the direction of groundwater flow (Bishop, *pers. comm.*, 1987; Edmunds *et al*., 1984). In addition, using the mineral saturation program WATEQF, Edmunds (1973) has demonstrated that the dissolved sulphide concentrations are too high for sulphate-sulphide equilibrium, suggesting that either additional redox reactions are involved or that kinetic factors have allowed non-equilibrium sulphide levels to accumulate. Thorstenson *et al*. (1979) consider bacterial sulphate reduction to be significant only on a geological timescale, therefore the low sulphate values encountered at depth probably represent the natural baseline levels for the aquifer which were prevalent prior to the influx of agrichemicals (Edmunds *et al*., 1984).

6.3.2.6. Methane/Hydrogen

An oily smell was detected instead of, or in addition to, the smell of sulphide in certain groundwater samples. These waters were from boreholes at least 29 km from outcrop, registering Eh values of +100 to -50 mV. Edmunds *et al*. (1984) also noted this phenomenon

but detected the oily odours in waters with Eh values below approximately -100 mV. They concluded that the most likely explanation was the production of methane and/or hydrogen by fermentation, which may act as a lower redox boundary limiting the release of iron into solution.

$$CH_2O + 1/2CO_2 \rightleftharpoons 1/2CH_4 + CO_2$$

Bishop (1988) has determined methane in the groundwaters up to a maximum of 2.3 mg l^{-1}, although he admits that due to difficulties inherent in the determination of dissolved gases, the values are probably an under-estimation of the true concentrations at depth.

6.3.2.7 Iodine

Iodine levels in the groundwaters increase from 5-10 mg l^{-1} in zone 1 to >500 mg l^{-1} in zone 4. Unlike chloride, bromide, lithium and boron etc., the increase in iodine concentrations does not commence at the zone 2/3 boundary but just 2 or 3 km downdip of the redox barrier, thus the increase in iodine concentrations with depth is not primarily attributable to mixing with saline water. In figure 6.9, iodine determinations are plotted versus Eh values for each site; the behaviour of the element is clearly controlled by redox processes. Iodine levels slowly increase as the redox potential decreases from +100 mV to 0 mV; however, once the latter value is attained, the increase in concentration is marked.

The average iodine concentrations of 1.59 and 4.4 mg kg^{-1} in carbonate and argillaceous rocks, respectively (Matthess, 1982), demonstrate that iodine is probably concentrated in the argillaceous limestones, Clipsham Member and Upper Estuarine Series samples. There tends to be a strong correlation between iodine and the organic content of marine sediments (Cosgrove, 1970), decomposition of the latter causing the release of iodine into solution. Figure

6.9 suggests that this phenomenon commences once Eh values in the groundwaters have dropped to between +100 and 0 mV.

6.3.2.8 Fluoride

The spatial behaviour of fluoride in the groundwaters is unlike that of the other halides, increasing from <0.2 mg l^{-1} in zone 1 to a maximum of 4.6 mg l^{-1} at 29-30 km from outcrop. In the saline zone, fluoride concentrations decrease to approach that of the seawater sample (1.7 mg l^{-1}). The overall distribution closely resembles that of bicarbonate.

The fluoride content of the aquifer would be expected to be in the range 112-560 mg kg^{-1} (the average for carbonate and argillaceous rocks; Matthess, 1982), with most contained in or adsorbed on the micas and clay minerals (Rankama and Sahama, 1950). Edmunds (1973) determined the fluoride content of oxidised and reduced samples of oolitic limestone from this aquifer (140 and 260 mg kg^{-1}), and demonstrated its correlation with total organic carbon (0.16 and 0.23%, respectively).

As the waters migrate downdip the initial release of fluoride into solution is primarily controlled by redox reactions. Figure 6.9 demonstrates an upper redox boundary for fluoride at +200 to +150 mV, coinciding with the boundaries of the oxygen/nitrate and iron/manganese reduction zones. Fluoride forms strong complexes with a number of metals including ferric iron. The rapid release of fluoride into solution is therefore probably controlled by the reduction of iron (III) fluoride complexes at +200 mV, as revealed by the strong correlation between both elements in uncontaminated samples from zone 2. Fluoride also forms strong complexes with aluminium and beryllium, which may become significant in limiting fluoride concentrations at depth, in the presence of increased concentrations of boron (Hem, 1970), and once the removal of iron by

sulphide precipitation has commenced.

The groundwater pH may also be a significant factor in fluoride behaviour. The ionic radii of the fluoride and hydroxyl ion are of similar size, facilitating fluoride substitution in crystal structures and at mineral surfaces. With increasing pH fluoride can be displaced; thus as the alkalinity of the groundwaters increases with depth, fluoride ions may be released in exchange for hydroxyl ions (Matthess, 1982), until complexing or some other process comes into play, to restrict their release.

6.3.3 Influence of geochemical abundance, adsorption and solubility controls on minor and trace element distributions

The influence of carbonate equilibria, ion exchange, mixing with saline water and redox controls on the distribution of major and minor elements in the groundwaters have been discussed. Many elements are maintained at very low levels due to their low abundance in the aquifer matrix itself; the release of others is limited by strong adsorption on organic matter, colloidal material, and/or clay minerals, by the low solubility of the minerals which dominate in the prevailing Eh/pH conditions, or by the formation of complexes which may be precipitated. Groups of elements are discussed in turn, with reference to these phenomena. As determinations of minor and trace elements can be invalidated by contamination, possible sources of contamination in the groundwaters are summarised.

6.3.3.1 Sources of Contamination

Trace elements that could not be quantified because they occurred at concentrations below the instrumental detection limit included beryllium, scandium, yttrium, vanadium, cobalt, chromium, zirconium, cadmium, molybdenum, lead and the lanthanides. Iron, manganese, copper, zinc and aluminium were detected in most samples,

Table 6.4

Mean concentrations of trace elements for 16 groundwater samples in which contamination is suspected and 33 'uncontaminated' groundwaters.

	*'Contaminated' samples			'Uncontaminated' samples		
	Minimum	Mean	Maximum	Minimum	Mean	Maximum
	concentrations ($\mu g\ l^{-1}$)			concentrations ($\mu g\ l^{-1}$)		
Iron	18.9	941	4050	<0.5	194	863
Manganese	0.6	8.5	25.4	<0.2	3.1	14.1
Copper	<0.3	4.6	43.3	<0.3	0.6	6.3
Zinc	2	91	629	<2	16.5	140
Aluminium	<5	14	111	<5	2.7	21

*Possible contamination is either due to dissolution of suspended material prior to filtration of the samples in the laboratory, or from borehole corrosion products.

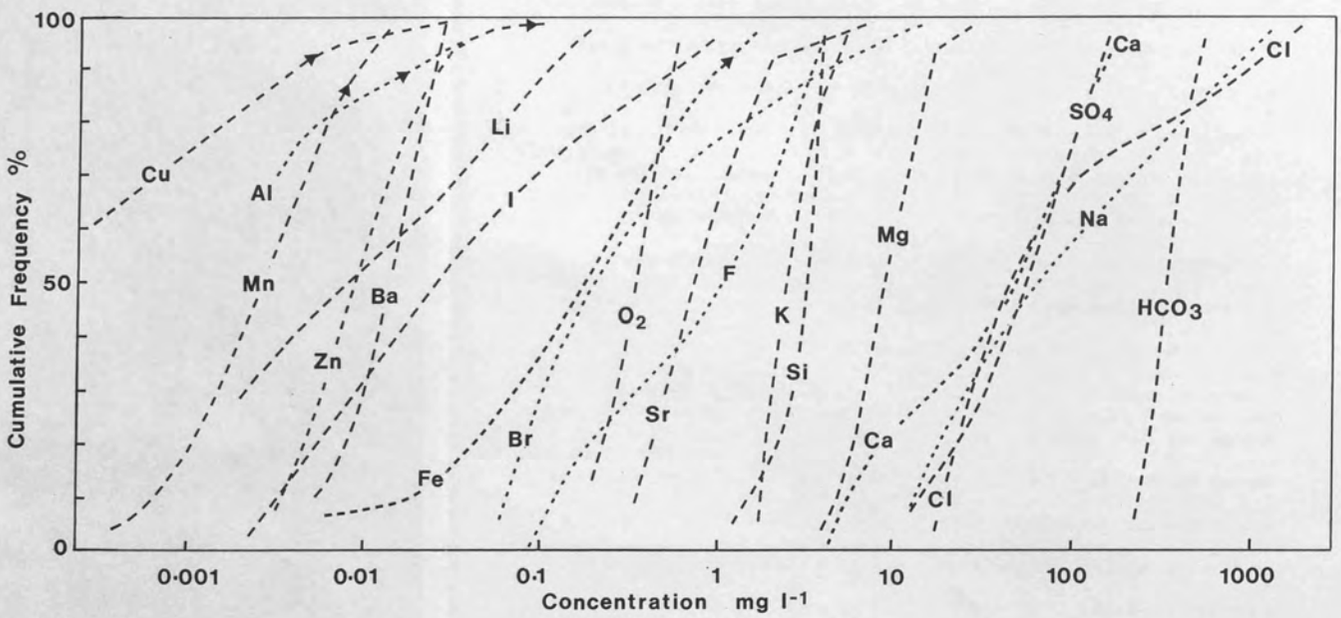
however, contamination from suspended material and/or borehole corrosion products is suspected in over one-third of the samples.

At sixteen sites, low artesian flow or the pipework arrangement precluded the determination of Eh, dissolved oxygen and the use of the on-line filtration unit; in view of the large volumes sampled, manual field-filtration was considered impracticable. During filtration in the laboratory, two to four weeks after sampling, iron hydroxides and clays were retained by the 0.45 µm filter for certain samples. However, it is likely that a proportion of the suspended material dissolved after acidification, to yield additional iron, titanium and aluminium etc. The worst case is exemplified by site 48 (Crowland Bridge), as a small influx of clay was noted towards the end of sampling, much of which "settled out" or was retained on the filter in the laboratory. There is considerable debate over the use of filters, and the arbitrary division of suspended and dissolved fractions in waters at 0.45 µm (2.2.2); however, all but three of the samples which contain aluminium, were not filtered on-site. The sample from Crowland Bridge has five times the aluminium and zinc concentration of the nearby Moulton West Fen (49) sample which was filtered in the field. Light rare earth elements, incorporated in clay mineral structures or tightly held at ion exchange sites under neutral/alkaline conditions (Brown, 1971) are released in solutions of lower pH, hence light REE contamination is suspected for site 48 (6.3.3.4). Samples where contamination from copper and lead pipework (sites 1 and 6) and galvanised tanks (6 and 19) is suspected, are included in this group of samples.

Three other groundwater samples included in the "contaminated" group (sites 13, 32 and 34), contain >1 mg l^{-1} iron, and in view of Eh/pH measurements, borehole corrosion is suspected.

Figure 6.12

Cumulative frequency curves for 20 elements in the Lincolnshire Limestone groundwaters. Arrows denote the mean concentrations of the set of contaminated waters.



This may also be a problem at other sites.

Precautions taken to minimise the risk of contamination through contact with sample storage containers, equipment and reagents, are described in 2.2.2

The mean values of contaminated waters can be compared with those in which contamination is not suspected (table 6.4). Data from both groups are included in cumulative frequency curves (figure 6.12) where the mean value of the contaminated group is denoted with an arrow; the closer the arrow is to the 90% line, the stronger the effect of contamination for that particular element. The majority of trace element determinations were below the appropriate LQDC, therefore most trace metals are not included in the figure.

6.3.3.2 Alkali metals

Sodium, potassium, lithium and rubidium were determined in both limestone and groundwater sample sets. Rubidium levels were below the detection limits of the residue method (which rose with increasing salinity from 2.5-13.7 $\mu g\ l^{-1}$), however, Edmunds (1973) obtained a limited number of rubidium and caesium determinations for the groundwaters in the 1-5 and 0.05-0.2 $\mu g\ l^{-1}$ ranges respectively.

The order of decreasing abundance for the alkali metals in the limestone samples is: K > Na > Li > Rb > Cs and in the groundwaters: Na > K > Li > Rb > Cs (table 6.5). On the basis of hydrated ionic radius, the order of replaceability should be Li < Na < K < Rb < Cs (6.2.4), thus caesium with an effectively smaller radius than the other elements, is adsorbed more strongly on clay minerals etc. From the order of replaceability **lithium** would be expected to be present as a major element, however it occurs at concentrations three orders of magnitude below those of **sodium**. The reasons for the preferential release of sodium ions into solution are two-fold: (1) as a marine sediment, ion exchange sites in the

Table 6.5

Group I and II metals in 18 rock and 49 groundwater samples from the Lincolnshire Limestone and one rock sample from the Upper Estuarine Series (B3).

	ROCK SAMPLES (mg kg^{-1})				GROUNDWATER SAMPLES (mg l^{-1})		
	LINCOLNSHIRE LIMESTONE			UES			
	Minimum	Mean	Maximum	B3	Minimum	Mean	Maximum
Na	96	356	2164	414	13	254	1949
K	125	984	4690	415	1.6	3.1	12.7
Li	2	5	16	71	0.002	0.015	0.116
Rb	<2	5	24	4	<0.003-<0.014		
Ca	9%	28%	37%	0.8%	4	62	157
Mg	2111	3934	9529	905	3.1	10	35
Sr	345	443	799	79	0.36	1.00	5.01
Ba	8	42	262	28	0.001	0.014	0.034
Be	n.d	n.d	n.d	n.d	-	<0.00005	-

Ca concentrations are reported on a weight percent basis in the rocks

clays and organic matter are swamped by sodium, whereas the lithium content of seawater is low (0.17 in comparison with 10800 mg l^{-1} Na), (2) the ionic radius of sodium (11.0 nm) is more compatible with that of calcium (10.8 nm) for substitution than with that of lithium (8.20 nm).

Potassium is released from clay minerals and organic matter with difficulty and therefore its spatial distribution in the groundwaters does not follow that of sodium. The Na/K ratio of 15-20 in zone 1 is typical of groundwaters close to the area of recharge (Matthess, 1982), and increases to greater than 300 in the saline waters; potassium concentrations decrease in zone 2, and only increase eastwards at a much slower rate than sodium. The restriction on potassium release could be its low abundance in the aquifer as its mean concentration in the limestone is <0.1% by weight, however it is more abundant than sodium. Clay minerals probably bring about the net removal of potassium from solution, although K^+ ions are large, they are readily incorporated into the inter-layer sites of illite, where they are likely to remain fixed rather than be exchanged further down the flow path (Matthess, 1982).

In natural waters the behaviour of **rubidium** and **caesium** tends to be similar to that of potassium; having even smaller hydrated ionic radii they are the least likely of the alkali metals to be released from clay minerals etc. This phenomenon coupled with the very low concentrations at which rubidium and caesium occur in the aquifer, restricts their abundance in the groundwaters.

The distribution of the alkali metals in the Lincolnshire Limestone groundwaters are influenced primarily by geochemical abundance and their ionic radii. The increase in concentrations of sodium, lithium and potassium (plus rubidium and caesium) commence

at 15, 20 and 25 km from outcrop respectively. Ion exchange for calcium initiates the rise in sodium levels, a process which leaves lithium concentrations unaffected. By the end of zone 2, the sodium-calcium ion exchange capacity of the aquifer is apparently exhausted (Lawrence *et al.*, 1976), and the influence of mixing with saline water increases, heralded by the initial increase of chloride and lithium. The larger alkali metals are retained more strongly by surface adsorption; their eastward increases commencing at approximately 24 km from outcrop, the easterly limit of public potable supply. In the saline zone (4), the concentration of all Group I elements probably increases as a function of time for rock-water contact compounded by membrane-filtration effects (6.4.2)

6.3.3.3 Alkaline earth elements

The order of replaceability in Group II metals is Mg < Ca < Sr < Ba (6.2.3); the order of decreasing concentration in groundwaters reflects that of the limestones: Ca < Mg < Sr < Ba (table 6.5).

Incongruent calcite dissolution is the primary source of **magnesium** and **strontium**, until surface adsorption and ion exchange processes dominate (from 25 km from outcrop); saturation indices (figure 5.11) demonstrate that the significance of strontianite, celestine and dolomite is negligible.

Calcium is the dominant member of this group of elements, that is, the anticipated order of magnesium and calcium are reversed. This is primarily due to geochemical abundance, calcium concentrations being two orders of magnitude greater than that of magnesium in the aquifer matrix, with a Ca:Mg ratio of 7:1. Carbonate equilibria (6.3.1.1) maintain calcium as the dominant cation close to outcrop (Ca:Mg ratio = 12:1), however, once the groundwaters are saturated with respect to calcite, and 60% of the

calcium has been removed by ion exchange, leaching from the rest of the aquifer matrix becomes important. The Ca:Mg ratio decreases from 6:1 in zone 3 to 1:1 in the saline waters of zone 4, and at two sites the magnesium concentration exceeds that of calcium. The groundwaters are greatly undersaturated with respect to hydrated magnesium hydroxides and oversaturated at depth with respect to dolomite, therefore the primary source of magnesium at depth is probably Mg^{2+} ions held by adsorption on clay minerals etc. As the concentrations of magnesium and calcium are 1290 and 410 mg l^{-1} respectively in seawater (Krauskopf, 1979), abundant magnesium should be available for release in the argillaceous members of the aquifer.

Barium has a large ionic radius which precludes its substitution for lighter alkaline earths in the lattices of calcium carbonates and sulphates. This is illustrated in figure 6.2 where a gradual decrease in barium concentration is observed as calcium levels in the rocks increase, unlike those of magnesium, strontium and manganese which remain relatively constant.

Barium levels in the groundwaters are low and in the narrow range 10-20 µg l^{-1}, attaining maximum concentrations in zones 2 and 3. The carbonate (witherite) is unlikely to control barium behaviour as (1) the groundwaters become increasingly undersaturated with respect to the mineral with depth (figure 5.11) and (2) witherite is exclusively a vein mineral and unlikely to occur in sediments; $BaSO_4$ is less soluble and the ratio of bicarbonate to sulphate ions is usually high enough to prevent the formation of the carbonate (Krauskopf, 1979). At sulphate concentrations of 10 and 100 mg l^{-1} SO_4, corresponding barium concentrations of the order of 140 and 14 µg l^{-1} respectively, would be anticipated (Hem, 1970). However, sulphate concentrations decrease from 150 mg l^{-1} near outcrop to

<10 mg l^{-1} at depth, while barium concentrations remain low. The presence of halides in zones 3 and 4 would tend to increase the solubility of $BaSO_4$, but an increase in barium concentrations is not apparent, except in the extreme south-east of the area. The groundwaters around Bourne are saturated with respect to barite but become increasingly undersaturated with respect to the mineral with depth; thus, while barite dissolution may control barium release in the unconfined zone, other processes such as ion-exchange may be more significant in the confined section of the aquifer.

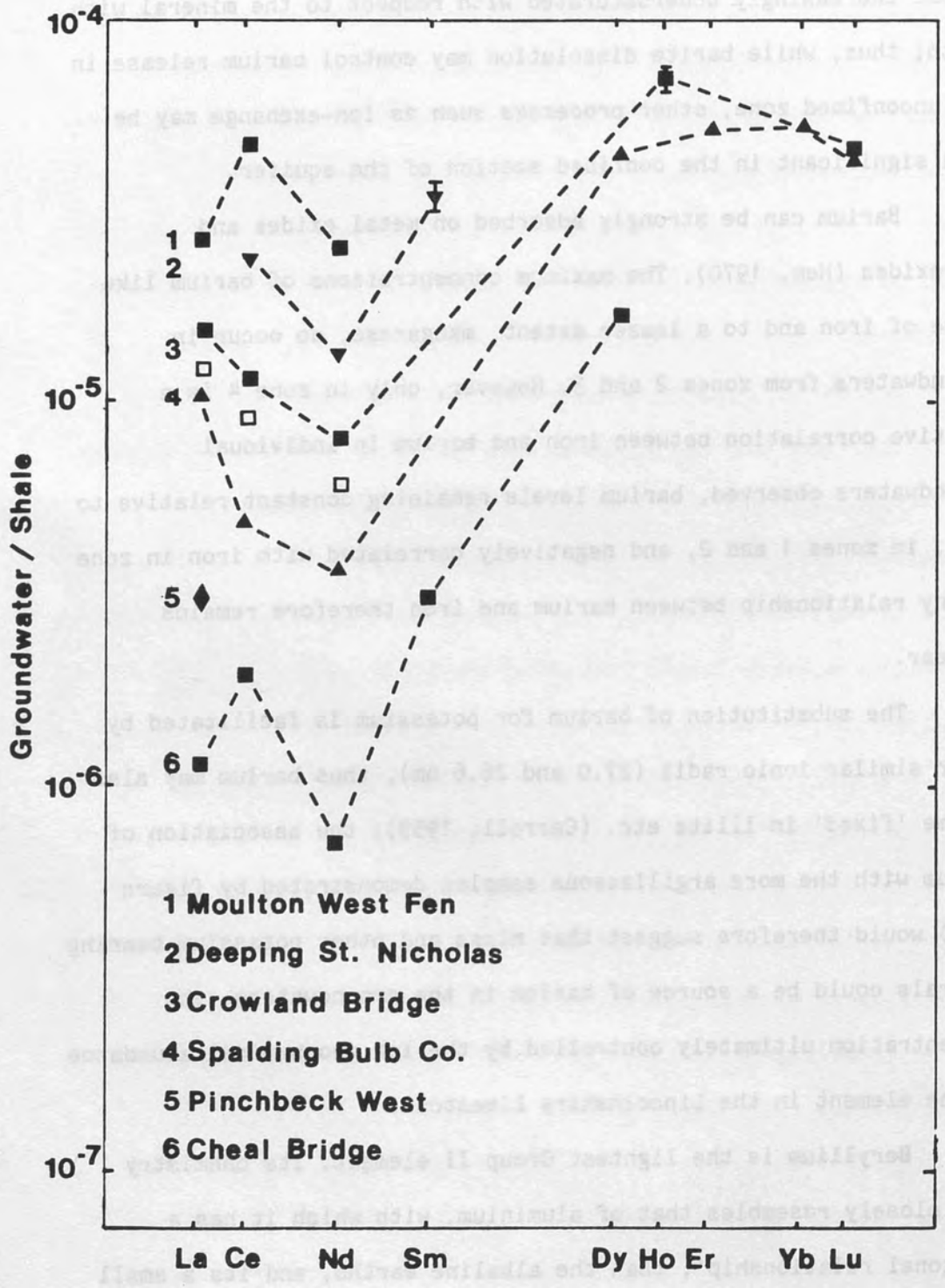
Barium can be strongly adsorbed on metal oxides and hydroxides (Hem, 1970). The maximum concentrations of barium like those of iron and to a lesser extent, manganese, do occur in groundwaters from zones 2 and 3. However, only in zone 4 is a positive correlation between iron and barium in individual groundwaters observed, barium levels remaining constant relative to iron, in zones 1 and 2, and negatively correlated with iron in zone 3. Any relationship between barium and iron therefore remains unclear.

The substitution of barium for potassium is facilitated by their similar ionic radii (27.0 and 26.6 nm), thus barium may also become 'fixed' in illite etc. (Carroll, 1959); the association of barium with the more argillaceous samples demonstrated by figure 6.2 would therefore suggest that micas and other potassium-bearing minerals could be a source of barium in the groundwaters, the concentration ultimately controlled by the low geochemical abundance of the element in the Lincolnshire Limestone.

Beryllium is the lightest Group II element. Its chemistry more closely resembles that of aluminium, with which it has a 'diagonal relationship', than the alkaline earths, and its a small ionic radius facilitates its substitution for silicon in igneous

Figue 6.13

Shale normalised rare earth element concentrations for six groundwaters from the saline zone. The open squares are probably more representative of the light REE values for the Crowland Bridge sample, allowing for possible contamination (see section 6.3.3.1)



minerals. The average beryllium concentrations reported for shales and carbonates are 6 and 0.7 μg l^{-1} respectively (Matthess, 1982) and concentrations in the groundwaters are consistently below the detection limit (0.05 μg l^{-1}). Like aluminium (6.3.3.6) therefore, the behaviour of beryllium is probably controlled by its low abundance in the limestone and the low solubilities of oxide and hydroxide phases, the presence of which are consistent with the pH conditions of this aquifer.

6.3.3.4 Group IIIB elements - Sc, Y and the REEs

The average **scandium** content of the limestones is 3 mg kg^{-1}, but the content is higher in the confining lithologies (maximum 26 mg kg^{-1}), due to its adsorption on clays, hydrous aluminium and ferrous oxides etc. Scandium concentrations in water are limited by its tendency to form hydroxide complexes of considerable stability, for example $[Sc(H_2O)_5OH]^{2+}$. It also complexes with sulphate, carbonate and bicarbonate ions (Frondel, 1970). The low concentrations (<0.05 μg l^{-1} Sc), reported in the dissolved, fraction are therefore restricted by its tendency to be precipitated, transported as complexes, or adsorbed on colloids.

The method for the determination of **rare earth elements** in the groundwaters is described in 4.3.3. Due to the very low levels of half of the REEs determined in the residues, only limited analyses for a few sites are considered reliable. Shale normalised abundances for five groundwater samples from the saline zone are plotted in figure 6.13 and reveal a strong heavy REE fractionation in the waters. The concentrations of REEs increase in the sample order:

Cheal Bridge =< Pinchbeck West < Spalding Bulb Co. =< Crowland Bridge < Deeping St. Nick < Moulton West Fen

Being trivalent the rare earth elements tend to be adsorbed in argillaceous sediments; however, during weathering they may enter

carbonate lattices by substitution for calcium (Rankama and Sahama, 1950). The total REE (La-Lu, + Y) content of the oolitic limestones ranges from 10-20 mg kg^{-1} for the purest samples, to 30-50 mg kg^{-1} for most of the argillaceous limestones; no fractionation is exhibited when compared with a standard shale. In comparison, the uppermost (Clipsham Member) and basal argillaceous limestones (500-930 mg kg^{-1}) and the Upper Estuarine Series samples (300-1300 mg kg^{-1}) exhibit strong heavy REE depletion, due to a combination of greater adsorbability of the light REEs on clay particles etc., and the tendency of heavy REEs to form soluble complexes (Herrman, 1970; Felsche, 1978).

Yttrium accounts for a large proportion of the total REE abundance quoted above, ranging from 0.3-7 mg kg^{-1} in the oolitic samples, to 59-68 mg kg^{-1} in the Clipsham Member and 27-84 mg kg^{-1} in the Upper Estuarine Series. In all the samples analysed, yttrium is considerably more abundant than scandium and the REEs.

Overall, the REE content available for leaching is small and limits absolute total REE concentrations to approximately 1 µg l^{-1}. As expected, the high solubility of heavy REE compounds and the adsorption of light REEs on suspended particles, causes heavy REE enrichment in the groundwaters.

Brookins (1983), demonstrated that the occurrence of a predominant REE species in seawater, is dependent only on the pH conditions (cerium and europium excepted). Thus, under moderately oxidising to moderately reducing conditions, the critical values in seawater are pH 7.5 (which separates the stability fields of aqueous trivalent species and the carbonate phases) and 8.5 (above which metal hydroxides are stable). This is the case for the middle REEs, the heavier elements have no stable carbonate phase under the experimental conditions imposed, and the light REEs no hydroxide

phase. Although Eh/pH conditions in seawater are similar to those prevalent in the groundwaters from the Lincolnshire Limestone, the ionic strengths and REE activities are higher, thus only generalisations on REE speciation can be applied to the groundwaters. From Brookins' Eh/pH diagrams it is clear that in zones 1-3, only the M^{3+} REE species are of significance, zone 4 being dominated by the carbonate and hydroxide phases of the light and heavy REEs respectively. For the middle REEs (samarium to dysprosium), the groundwaters pass through the stability fields of three phases, the transition between M^{3+}, carbonate and hydroxide phases occurring between zones 2 and 4, depending on the element. The stability fields of yttrium species are similar to those of the light REEs.

Cerium is an exception in this discussion, as the redox potential as well as the pH are of significance in its speciation. The cerium depletion exhibited by seawater is caused by its oxidation from the trivalent state to Ce^{4+}, and subsequent precipitation as ceric oxide (Carpenter and Grant, 1967). Brookins' (1983) data show that this can occur in even the reducing groundwaters of the saline zone, as they are sufficiently alkaline to place them within the stability field of CeO_2. Thus, unless any kinetic factors delay the reaction, cerium depletion relative to the other light REEs should be observed in the groundwaters. Of the four residue samples for which lanthanum, cerium and neodymium determinations are available, the relative concentrations of the light REEs follow inconsistent trends. Praseodymium is a nearer neighbour to cerium than neodymium; however, all determinations of the element are below detection limit levels, which are up to an order of magnitude greater than the reported concentrations of the

Table 6.6

Trace metals in the rocks and groundwaters of the Lincolnshire Limestone and Upper Estuarine Series (UES).

	ROCK SAMPLES			GROUNDWATERS	
	LINCOLNSHIRE LIMESTONE			U.E.S	
	Minimum	Mean	Maximum	(Sample B3)	Mean
Al	582	3493	12965	24343	2.7
Co	13	16	25	11	<0.8
Cr	<5	12	36	63	<1
Cd	n.d	-	-	-	<1 (<0.2 - <3)
Cu	12	14	17	9	0.6
Fe	1784	5443	15737	5805	194
Mn	<155	187	465	<155	3.1
Mo	<9	<9	15	<9	<2
Nb	14	16	19	20	<1.5 - <13.7
Ni	36	43	70	50	<1
Pb	n.d	-	-	-	<10 (<5 - <17)
Sc	2	6	26	17	<0.05
Ti	<120	620	2640	4796	<155 - <2063
V	13	28	56	124	<0.2
Y	0.3	12	68	84	<0.05
Zn	<5	<5	11	38	16.5
Zr	<3	67	464	683	<0.5

Cd, Nb, Pb and Ti determinations of the groundwaters were obtained by the "residue method", (see 4.3) The LQDC for each element increased with increasing total mineralisation.

Units of concentration - rocks: mg kg^{-1}, waters: µg l^{-1}

other light REEs. The determination of praseodymium may/may not permit the relative depletion of cerium in the groundwaters to be ascertained; however, trends in the available shale-normalised REE data are inconclusive in this respect.

6.3.3.5 Heavy metals

Titanium and **zirconium** are both concentrated in resistant accessory minerals (rutile and zircon etc.), hence the maximum concentrations (1.1% Ti and 856 mg kg^{-1} Zr) were determined in a silty sandstone from the Upper Estuarine Series (Sample M1). Structural titanium is released during the hydrolysis of pyroxenes, amphiboles and micas, and even zircon is susceptible to gradual attack, facilitating their concentration in "hydrolysate" sediments by adsorption (Rankama and Sahama, 1950; Erlank *et al.*, 1978). Argillaceous samples from the Upper Estuarine Series and Lincolnshire Limestone are therefore relatively enriched in both elements (0.5% Ti, 85-683 mg kg^{-1} Zr) in comparison with the oolitic limestones, for which determinations were below the limits of detection (120 and 3 mg kg^{-1} respectively).

Concentrations of these elements are also below detection limit levels in the groundwaters (0.15 mg l^{-1} Ti and 0.5 µg l^{-1} Zr, table 6.6), zirconium being limited primarily by low geochemical abundance. The detection limit for titanium is high, (see section 4.3), maximum concentrations would be expected to be approximately 1 µg l^{-1}, limited by the solubility of $TiOOH^{+}$ (Hem, 1970).

Under the prevailing Eh/pH conditions, the **vanadium** species most likely to be present in the groundwaters are 3- and 4-valent, with a minimum solubility of 1 µg l^{-1} (Hem, 1970). In aerated waters the solubility of vanadium species is increased, thus the only four samples containing detectable vanadium (>0.2 µg l^{-1}) also contain detectable traces of dissolved oxygen (>0.2 mg l^{-1}). These

determinations do not exceed 1 μg l^{-1}, however, probably because the element tends to be removed in oxygenated waters by freshly precipitated ferric hydroxide (Krauskopf, 1956). It is unlikely that any vanadium species could approach saturation in any of the groundwaters, as only 13-56 mg kg^{-1} is available in the limestone (table 6.6).

An average reported concentration for shales of 15 mg kg^{-1} Nb (Krauskopf, 1979) and an average seawater concentration of 0.01 μg l^{-1} (Brewer, 1975), indicate the low abundance and mobility of **niobium**. Determinations for the Lincolnshire Limestone samples are primarily in the narrow range 14-20 mg kg^{-1} Nb, with a tendency for the higher concentrations to occur in the argillaceous samples, where it probably occurs as oxides and hydroxides (Wedepohl, 1978). Niobium salts are readily hydrolysed and adsorbed in shales etc. The element is often closely associated with titanium and zirconium in resistant accessory minerals (Rankama and Sahama, 1950), the maximum concentration (31 mg kg^{-1} Nb) in a silty sandstone from the Upper Estuarine Series is coincident with the maximum concentrations of those two elements. The detection limits for the determination of niobium in the groundwater residues (4.3) increase with salinity from 1 to 8 μg l^{-1} and were consistently higher than the levels of niobium in the groundwaters. The element is probably present as Nb^{3+} in the groundwaters (Wedepohl, 1978).

The geochemically similar **cobalt** and **nickel** occur at approximately 15 and 40 mg kg^{-1} respectively in the main body of the limestone, slightly higher (25 and 70 mg kg^{-1}) in the argillaceous lithologies confining it. Both elements are maintained at concentrations below 1 μg l^{-1} in the waters. In the divalent state, at a pH of 8 and bicarbonate concentration of only 100 mg l^{-1} (the minimum in the Lincolnshire Limestone waters), the solubility of

$CoCO_3$ restricts cobalt activity to 10^{-7}M (Matthess, 1982) i.e. 6 $\mu g\ l^{-1}$, the solubility of $NiCO_3$ is greater, but still less than that of siderite. Both elements are strongly adsorbed by hydrous iron and manganese oxides (Krauskopf, 1956). The natural concentrations of nickel and cobalt are therefore limited by a combination of low geochemical abundance, adsorption and low solubility of the carbonates. Adsorption on colloids and availability in the limestone (<9 mg kg^{-1}) are also responsible for the non-detection of **molybdenum** (<2 $\mu g\ l^{-1}$). Ocurring probably as the anionic molybdate (Hem, 1970), it is very unlikely that effective solubility controls limit its abundance.

The average concentration of **chromium** in the Lincolnshire Limestone is 11 mg kg^{-1} most of which is probably associated with detrital material (Shiraki, 1978) many samples containing <5 mg kg^{-1}; up to 100 mg kg^{-1} is available in the overlying lithologies. Chromium determinations in the groundwaters are consistently below the detection limit (1 $\mu g\ l^{-1}$ Cr), although chromium solubility controls would limit concentrations to <0.5 $\mu g\ l^{-1}$ (Hem, 1970). Adsorption on MnO_2 may also be a significant factor in limiting chromium concentrations in samples from close to the redox barrier.

In the purest oolitic limestones **iron** concentrations occur in the 0.18-0.25% range, rising to 0.9% in the Clipsham Member and 15.7% in the basal Upper Estuarine Series sample. **Manganese** concentrations are at or below detection limit levels (155 mg kg^{-1}), with a maximum of 465 mg kg^{-1} in the Clipsham Member. Most of the iron and manganese is incorporated in micas and clay minerals, the hydroxide films coating them, or in the carbonate lattice itself (6.2). Although much of the iron and manganese is probably derived from the Lincolnshire Limestone, the underlying lithologies may have

been an additional source, in particular the Northampton Sand, from which siderite has been extracted commercially. At some stage in the depositional and/or diagenetic history of the middle and upper Jurassic sequence, iron-rich fluids from the Northampton Sand would have migrated under pressure through the Grantham Formation (which is thin or even absent in south Lincolnshire), upwards through the overlying sequence. If the Upper Estuarine Series had become compacted by this time, some of the fluid could have been retained in the Lincolnshire Limestone itself.

The average concentrations of the uncontaminated groundwaters are 194 and 3 $\mu g\ l^{-1}$ iron and manganese respectively (table 6.6). Redox reactions, the primary control on the distributions of these elements are discussed in 6.3.2.3: the precipitation of $Fe(OH)_3$ and MnO_2 and FeS restrict their activity in aerated waters and at depth, respectively. The release of iron and manganese into solution is limited to groundwaters with Eh values in the approximate range +300 to -150 mV (manganese) and +150 to -100 mV (iron), the latter corresponding approximately to groundwaters in zone 2.

Copper determinations for the limestone and Upper Estuarine Series exhibit no correlation with lithology and are in the narrow range 10-17 $mg\ kg^{-1}$. The amount available for leaching by the porewaters is therefore limited. In aerated waters, cupric oxide or hydrocarbonate minerals limit the solubility of copper at neutral pH to $10^{-6}M$ (64 $\mu g\ l^{-1}$) and at pH 8, to 6.4 $\mu g\ l^{-1}$ (Hem, 1970). However, copper solubilities are decreased under reducing conditions, particularly if sulphide species are present; thus the mean concentration of uncontaminated groundwaters from the Lincolnshire Limestone is only 0.6 $\mu g\ l^{-1}$, most samples containing $<0.3\ \mu g\ l^{-1}$. Determinations in excess of 1 $\mu g\ l^{-1}$ were only obtained from uncontaminated sites with positive Eh values and pH <8 .

The distribution of **zinc** is usually controlled by the solubilities of the carbonate and sulphide. However, in the Lincolnshire Limestone, adsorption on iron and manganese in the oxidised waters (Krauskopf, 1956), complexation with organic matter and clay minerals, and its low abundance in the aquifer are probably of greater significance in maintaining low levels in the groundwaters. Most samples contain <5 mg kg^{-1} Zn, with a maximum of 11 and 38 mg kg^{-1} in the argillaceous limestones and Upper Estuarine Series sample, respectively. Half of the groundwaters contain <10 µg l^{-1}, and for most samples in which concentrations greater than 50 µg l^{-1} were reported, contamination is suspected.

Cadmium is frequently associated with zinc, but is geochemically rare, average carbonate and shale concentrations being 48 and 180 µg kg^{-1} respectively (Matthess, 1982). All the water samples contained <1 µg l^{-1} although the least saline samples can be reported as <0.2 - <0.4 µg l^{-1}. In these limestone groundwaters, Cd^{2+} is the dominant species; complexes with ammonium, cyanide and halides are known (Wakita, 1970), however, its abundance is probably controlled by the solubilities of the carbonate and sulphate (Matthess, 1982). In the aerated samples, its abundance may also be limited by adsorption on MnO_2 (Krauskopf, 1956).

The low geochemical mobility and solubility of **lead** and its minerals restrict concentrations to below ICP-OES detection limits. An average lead concentration of 16.5 mg kg^{-1} was reported for carbonates by Matthess (1982); Wedepohl (1974) quoted an average concentration for limestones of 5 mg kg^{-1} of which 3 mg kg^{-1} was contained in the 10-15% clay and silt fraction. In the waters, lead would be expected to be present as Pb^{2+} (Garrels and Christ, 1981), and its activity to be limited by the solubilities of cerrusite (carbonate) and anglesite (sulphate) in oxidised waters, and galena

(sulphide) in reducing samples to 10^{-8}M (Hem, 1970) or approximately 2 µg l^{-1}. Using AAS and the residue preconcentration method all groundwater samples were found to contain < 3 µg l^{-1}. Lower detection limits were obtainable on the lower TDS samples from zone 3, these had concentrations below 0.2 µg l^{-1}. Like copper and zinc, lead is strongly adsorbed on hydrated MnO_2 and $Fe(OH)_3$ (Krauskopf, 1956), which may be a significant limiting factor in the most westerly sites.

6.3.3.6 Aluminium

Aluminium is the third most abundant element in the aquifer. The average concentration of the eighteen typical limestone samples is 0.3%, and the Clipsham Member (B4) contains 13%. The clay mineralogy of the Lincolnshire Limestone is dominated by kaolinite, which should restrict the aluminium concentration to 21%; however, sample B3 (basal Upper Estuarine Series sample) contains 25%. High aluminium concentrations are facilitated by the alteration of the clays and/or the direct precipitation of aluminium hydroxide, the aluminium concentrations of gibbsite and boehmite being 34.6% and 45% respectively (Hem, 1970b; Degens, 1965).

Although a significant amount of aluminium is present in the agillaceous lithologies, and even the purest oolitic samples contain 500 mg kg^{-1} Al, most of the groundwaters contain <5 µg l^{-1}. A principal control is pH, which is effectively buffered by the limestone above 7. The pH conditions required for the hydrolysis of kaolinite (the primary source of aluminium in the Lincolnshire Limestone) are less than 5. Most other common aluminium-bearing minerals which dissolve reversibly have low solubilities in the pH range of natural waters, while those dissolving irreversibly do so extremely slowly (Hem, 1970b), therefore, only the samples which were acidified (pH 2) prior to filtration contain high levels of

Table 6.7

Anions in 18 rock and 49 groundwater samples from the Lincolnshire Limestone and one rock sample from the Upper Estuarine Series (B3). For elements which were not determined in the rock samples, published values for average carbonates and shales (Matthess, 1982) are presented.

	ROCK SAMPLES (mg kg^{-1})				GROUNDWATER SAMPLES (mg l^{-1})		
	LINCOLNSHIRE LIMESTONE			UES			
	Minimum	Mean	Maximum		Minimum	Mean	Maximum
*Si	0.23%	8.55%	50%	85%	1.0	3.2	4.2
P	<44	<44	109	109	0.041	0.286	1.10
	Average Carbonates		Average Shales				
B	16		194		0.031	0.821	3.33
NO3-N	-		-		<0.1	0.6	5.3
S	1850		4550		<0.2	23	55
Cl	170		305		21	275	2960
F	560		112		0.095	1.51	4.600
Br	4.3		6.6		0.072	1.25	15.50
I	4.4		1.6		0.003	0.167	1.63

* Si concentrations in the rock samples are reported on a weight percent basis

aluminium, released from suspended clay particles during storage etc., these account for the majority of the "contaminated" waters (6.3.3.1).

Strong complexes with fluoride increase the solubility of aluminium, however, at the pH range of the Lincolnshire Limestone groundwaters (pH 7-9), flouride concentrations (generally <1 mg l^{-1}) would have to be an order of magnitude higher to have a significant effect on aluminium levels. Similarly, sulfate complexes in the presence of fluoride at such low levels, could only raise dissolved aluminium concentrations in acid waters (Hem, 1970b). Poorly crystallised clay minerals and gibbsite tend to form, if silicon is present at concentrations slightly above or slightly below 2 mg l^{-1} Si, respectively (Matthess, 1982). Gibbsite crystals may be only be 0.1 µm in diameter and can therefore pass through the pores of a 0.45 µm filter and release aluminium on acidification. The precipitation of these phases would not appear to limit aluminium levels in the Lincolnshire Limestone groundwaters. With depth the waters become increasingly undersaturated with respect to amorphous $Al(OH)_3$, gibbsite, diaspore (and its polymorph boehmite) and the clay minerals. Saturation is only approached with respect to the partially hydrated phases in zones 1 and 2.

6.3.3.7 Minor anions

The **boron** determination reported by Harder (1973) for a German Jurassic oolite was 20 mg kg^{-1}; the average boron compositions of carbonate and argillacous rocks are 20 and 100 mg kg^{-1} respectively (Krauskopf, 1979). Grain size separations of rocks indicate two maxima for boron concentrations, one in the true clay size fraction (<2 µm) and a smaller peak at approximately 20 µm, which is probably partially traceable to tourmaline (Ernst, 1970). However, if tourmaline is present in the Lincolnshire

Limestone it is unlikely to have been broken down, most of the boron is probably incorporated in the clay content, particular in illite and micas (Matthess, 1982). Both illite and biotite have been identified in argillaceous lithologies within the aquifer, however, when magnesium is present (either in solution or on the surface of the clays), the uptake rate for the element is increased and it becomes 'fixed', probably as magnesium borate (Harder, 1973). The boron available for dissolution from the limestone and release into the groundwaters is therefore restricted.

The groundwater determinations are reported as total boron in the 0.03-5 mg l^{-1} range, however, boron is present in natural waters primarily as orthoboric acid, which dissociates with rising pH. At pH 8.2 (that is, waters at least 30km from outcrop), the ratio of H_3BO_3 (aq) to $H_2BO_3^-$ is 10:1 (Hem, 1970). The groundwaters become progressively enriched in boron with depth, the seawater/groundwater boron ratios decreasing from 4 to 0.5 within the saline zone. This eastward rise in concentration is probably a function of the increased residence time of the porewaters in the rock and membrane-filtration (6.4).

Silicon is the second most abundant element in the aquifer. The mean concentration of eighteen limestone samples is 4%, and it is further enriched in the argillaceous samples (up to 40%), bound up in clay minerals, micas, feldspars etc., and free silica. The latter is present as detrital quartz and secondary quartz and as amorphous silica in the form of siliceous skeletal material and cement.

The range of silicon concentrations in the groundwaters is narrow with a mean concentration of 3.4 mg l^{-1}; the highest concentrations (3.5-4.2 mg l^{-1}) are in groundwaters from zones 2 and 3. In the pH range of this aquifer, silicon would be expected to be

present as hydrated monomeric silicic acid (Hem, 1970), formed according to the reaction:

$$SiO_2\ \text{amorph} + 2H_2O \longrightarrow H_4SiO_4\ \text{aq}$$

However, this reaction proceeds only at very slow rates and solutions may remain undersaturated with respect to amorphous silica for a long time. Undersaturation of all the groundwaters with respect to chalcedony and silica gel is therefore observed (figure 5.11). Saturation indices also indicate that quartz saturation obtains in the north and in the saline zone, checking further silicon increases in these areas.

Phosphorus is only a minor element in the Lincolnshire Limestone aquifer. Determinations for the limestones are consistently below the detection limit (<44 mg kg^{-1}) only the Clipsham Member contains approximately 100 mg kg^{-1} P. By comparison an oolitic limestone from the Blisworth Limestone contains 175 mg kg^{-1} and the shell bed from the Upper Estuarine Series, 437 mg kg^{-1}; however, even these are relatively depleted in comparison with the average composition of carbonate (281 mg kg^{-1}) and argillaceous rocks (733 mg kg^{-1}) (Matthess, 1982). Apatite is the most common source of phosphorus in sediments, usually of an intermediate composition between the two end-members fluorapatite [$Ca_5(PO_4)_3F$] and hydoxyapatite [$Ca_5(PO_4)_3OH$] (Krauskopf, 1979). When attacked by water, the liberated phosphorus species are thought to recombine rather rapidly to form other minerals, or are adsorbed on clay minerals etc. (Hem, 1970). Like calcium carbonate the precipitation of apatite is favoured by warm, alkaline conditions, although a narrow, slightly lower pH range and more vigorous organic activity are required (Krauskopf, 1979). The low phosphorus content of the Lincolnshire Limestone would tend to indicate the absence of such ideal conditions during its deposition and/or diagenesis.

In zones 1 and 2, the phosphorus levels in the groundwaters are constant at 0.1-0.2 mg l^{-1}, however, the concentrations double in both zones 3 and 4, attaining 1.1 mg l^{-1} at site 49. The initial increase at 25 km from outcrop is concurrent with that of potassium, lithium, boron, bromide and chloride and thus probably attributable to mixing with saline water. The species prevalent up to 30 km from outcrop is $H_2PO_4^-$; within zone 4 the pH is at least 8, therefore $H_2PO_4^{2-}$ dominates. Like nitrogen, phosphorus has a variety of oxidation states, making it difficult to calculate solubility controls over phosphorus activity, however, the +5 state is probably the most common (Hem, 1970). The solubility of phosphorus does not seem to be influenced by hydoxyapatite, vivianite (a group of hydrous metal phosphates) or manganese orthophosphate, as levels of the element continue to rise after the waters have become oversaturated with respect to these minerals (figure 5.11); consistent undersaturation with respect to strengite [$FePO_4.2H_2O$] precludes its possible control.

Phosphate is the principal anion adsorbed by clay minerals, it is also fixed by the formation of insoluble salts of the alkaline earths, aluminium and iron (Carroll, 1959). The formation of the latter are favoured by acid conditions, therefore adsorption on clay minerals and the formation, at pH > 7.2, of phosphato calcium and magnesium complexes (Koritnig, 1978), may limit phosphorus levels in the groundwaters. Once mixing with saline water has commenced, desorption of phosphate ions presumably occurs, the potential amount available for release being restricted by the low geochemical abundance of the element.

Arsenic was not determined during the present investigation, however, BGS determinations of samples collected in 1983, were all below the detection limit (<4 µg l^{-1} As). The concentration of

arsenic in the groundwaters is probably restricted by a combination of low geochemical abundance (average contents of carbonate and argillaceous rocks are 1.75 and 9 mg kg^{-1} As respectively); adsorption on $Fe(OH)_3$ and MnO_2 (in the oxidising waters) and the low solubility of arsenic minerals, particularly in the presence of traces of heavy metals (Matthess, 1982). At pH > 7.2, the $HAsO_4^{2-}$ ion predominates, and in waters where Eh < +50 mV, $HAsO_2$ (aq) is prevalent (Hem, 1970).

The order of increasing abundance for the halides in groundwaters from zones 1 and 4, respectively, are I < Br < F < Cl and I < F < Br < Cl. As discussed in 6.3.1.3, the rapid increase in **chloride** and **bromide** concentrations at 20 km from outcrop, concurrent with the rise in lithium etc., is attributable to mixing with saline water. However, the distributions of **fluoride** and **iodine** are controlled by redox processes; the initial release of these elements from organic matter, colloidal material, iron oxides and/or clay minerals, coincides with a specific range of Eh values (6.3.2). In zones 2 and 3, in the south of the sampling area further release of fluoride is checked as saturation with respect to fluorite is approached (figure 5.11).

6.3.4 Temporal hydrochemical trends

A balance was maintained between abstraction for agricultural and domestic purposes and recharge, until large-bore pumping stations were constructed for public supply. Since the late 1960's-early 1970's, over-abstraction has resulted in a lowering of the water-table in the unconfined section of the aquifer, and capture of surface water at outcrop during periods of low stream-flow, causing a deterioration in water quality. In addition, zones of depression in the piezometric surface around principal abstraction sites have expanded (Burgess and Smith, 1979) causing the updip migration of

saline water at some easterly sites (also see 1.3.1.)

Data published by Edmunds and Walton (1983) for the period 1969/70 to 1979/80, and subsequent analyses (1982, BGS and 1985, this study), are used to identify temporal trends in the major ion chemistry of the groundwaters. Fluctuations in the salinity of the western groundwaters of the southern Lincolnshire Limestone is observed and in the waters further updip, the concentrations of a several ions are seen to increase with time.

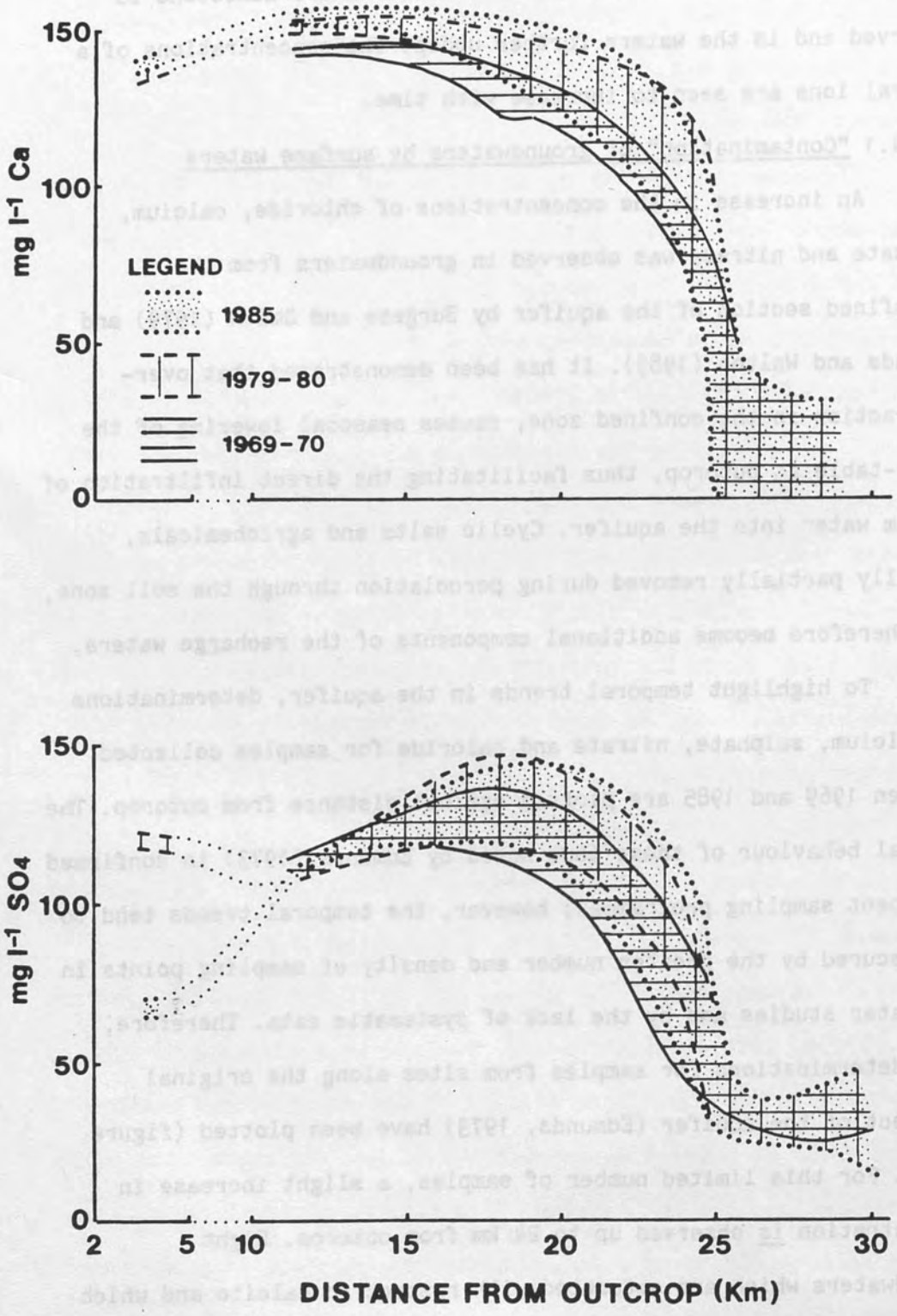
6.3.4.1 "Contamination" of groundwaters by surface waters

An increase in the concentrations of chloride, calcium, sulphate and nitrate was observed in groundwaters from the unconfined section of the aquifer by Burgess and Smith (1979) and Edmunds and Walton (1983). It has been demonstrated that over-abstraction in the confined zone, causes seasonal lowering of the water-table at outcrop, thus facilitating the direct infiltration of stream water into the aquifer. Cyclic salts and agrichemicals, normally partially removed during percolation through the soil zone, may therefore become additional components of the recharge waters.

To highlight temporal trends in the aquifer, determinations of calcium, sulphate, nitrate and chloride for samples collected between 1969 and 1985 are plotted against distance from outcrop. The spatial behaviour of these ions noted by Edmunds (1973) is confirmed by recent sampling programmes; however, the temporal trends tend to be obscured by the greater number and density of sampling points in the later studies and by the lack of systematic data. Therefore, only determinations for samples from sites along the original transect of the aquifer (Edmunds, 1973) have been plotted (figure 6.14). For this limited number of samples, a slight increase in concentration is observed up to 24 km from outcrop. Eight groundwaters which are saturated with respect to calcite and which

Figure 6.14

Determinations of calcium, sulphate, chloride and nitrate against distance from outcrop between 1969 and 1985.



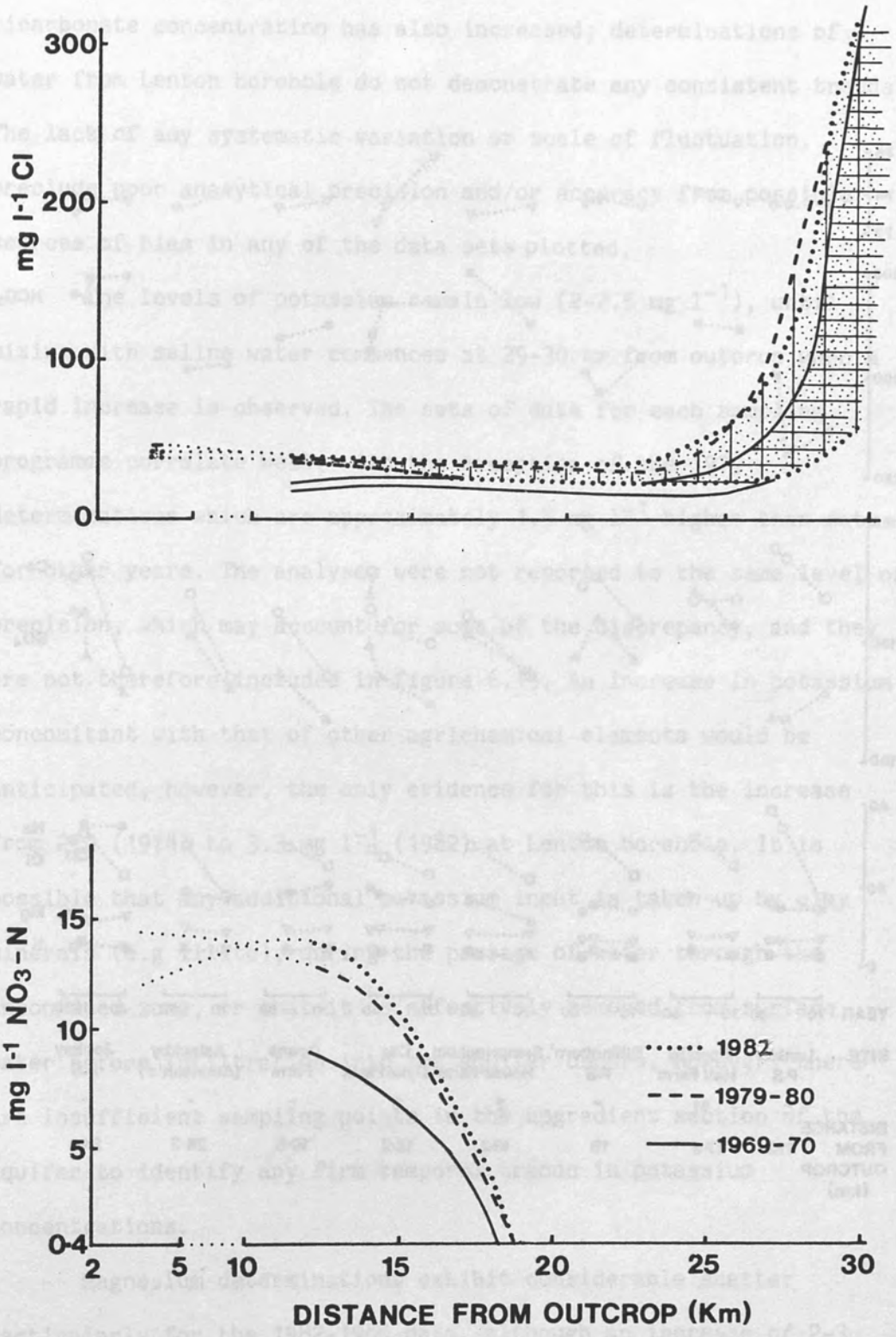
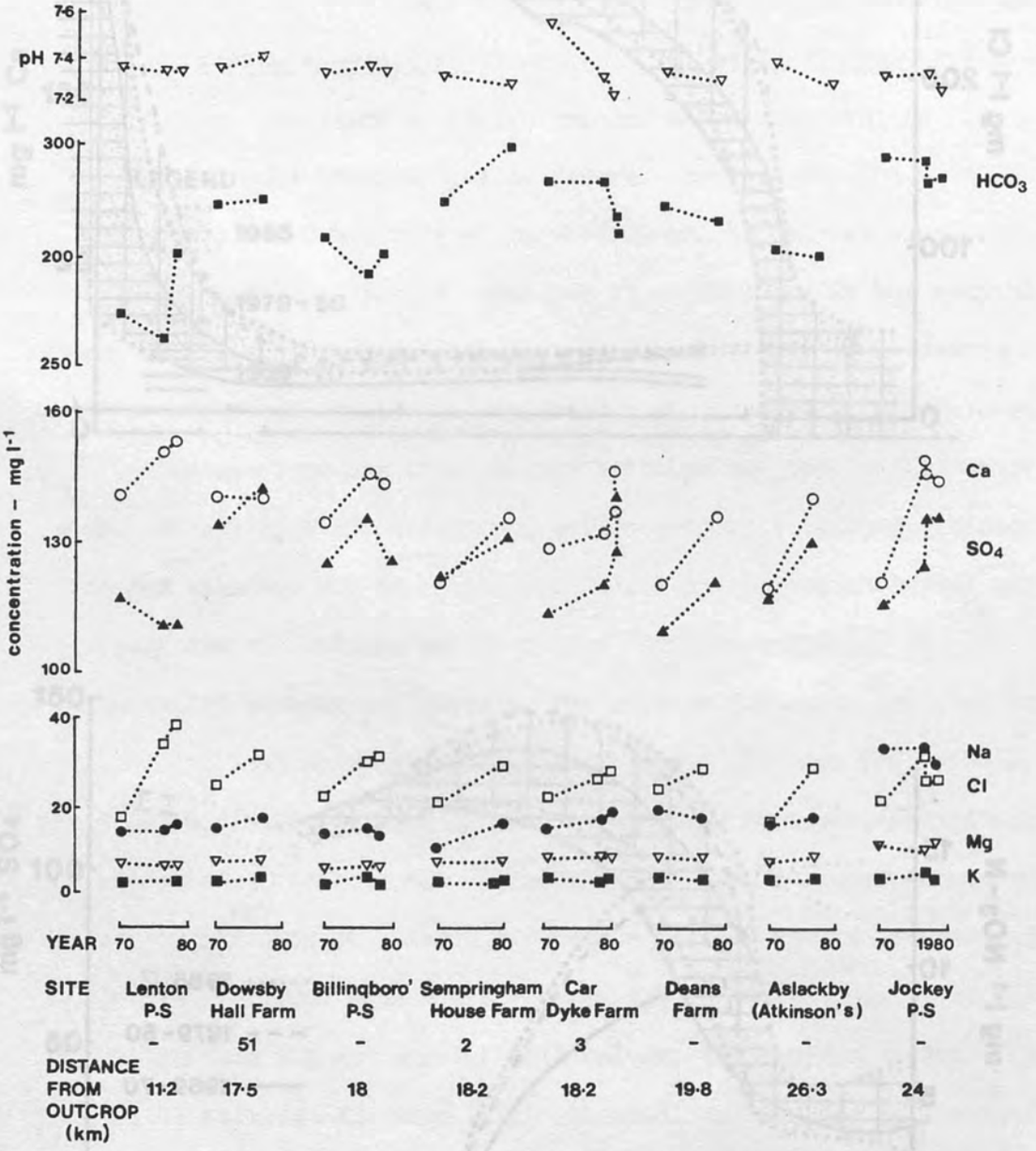

300
200
100
0
mg l-1 Cl
15
10
5
0·4
mg l-1 NO3-N
2
5
10
15
20
25
30
DISTANCE FROM OUTCROP (Km)
1982
1979-80
1969-70

Figure 6.15

Variations in pH and major ion concentrations in groundwaters from zones 1 and 2, collected between 1969 and 1985. Dates of sampling: June 1969/April 1970, April 1979/January 1980, January 1982/January 1983 (all BGS analyses), March and December 1985 (this study). Where appropriate, site numbers correspond to those in appendix 4.
The distance of each site from outcrop is calculated along the line of section shown in fig. 5.1.



have been sampled at least twice in the 1969-1985 period (figure 6.15), demonstrate that an overall increase of 5-20 mg l^{-1} in calcium and 5-15 mg l^{-1} in sulphate concentrations (i.e. an average of approximately 10%) has occurred while a decrease is observed in bicarbonate concentration and pH. Site 2 is exceptional as the bicarbonate concentration has also increased; determinations of water from Lenton borehole do not demonstrate any consistent trends. The lack of any systematic variation or scale of fluctuation, preclude poor analytical precision and/or accuracy from possible sources of bias in any of the data sets plotted.

The levels of potassium remain low (2-2.5 mg l^{-1}), until mixing with saline water commences at 29-30 km from outcrop when a rapid increase is observed. The sets of data for each sampling programme correlate well, with the exception of the 1979 determinations which are approximately 1.5 mg l^{-1} higher than data for other years. The analyses were not reported to the same level of precision, which may account for some of the discrepancy, and they are not therefore included in figure 6.15. An increase in potassium concomitant with that of other agrichemical elements would be anticipated, however, the only evidence for this is the increase from 2.2 (1974) to 3.3 mg l^{-1} (1982) at Lenton borehole. It is possible that any additional potassium input is taken up by clay minerals (e.g illite), during the passage of water through the unconfined zone, or that it is effectively removed from surface water before infiltration into the aquifer occurs. However, there are insufficient sampling points in the upgradient section of the aquifer to identify any firm temporal trends in potassium concentrations.

Magnesium determinations exhibit considerable scatter particularly for the 1982-1985 data, although an increase of 2-3

mg l^{-1} appears to have taken place over the years, down to 25 km from outcrop. However, nitrates are potential agrichemical pollutants of greater concern. An increase in nitrate concentrations at Lenton pumping station, 11 km from outcrop is apparent, with determinations of 9, 14.5 and 13 mg l^{-1} NO_3-N recorded for June 1969, April 1979 and January 1982 respectively. In general a slight increase along the original transect is observed, although nitrate levels fall below the limit of detection (0.4 mg l^{-1}) at 18.5 km (the redox barrier) in each data set.

Between 15 and 20 km from outcrop, sodium concentrations gradually increase due to ion exchange for calcium; meanwhile, chloride concentrations are maintained at a constant level (25-30 mg l^{-1}), until mixing with saline water becomes significant at 25 km from outcrop (6.3.1.3.). Since 1969 the increase in chloride levels in the first 20 km has been marked (5-10 mg l^{-1}), while sodium concentrations have increased by only 1-2 mg l^{-1} (figure 6.14). The main sources of chloride are minor concentrations in the limestone itself (probably no more than 200 mg kg^{-1}) and cyclic salts. The concentration of chloride in precipitation falling on the Lincolnshire Limestone is 5-7 mg l^{-1} (Downing and Williams, 1969), which is probably increased by evaporation, and by the influx of road salt in the winter months. The direct infiltration of precipitation and stream water during periods of low flow, is the most likely explanation for its slight increase since 1969.

Groundwater from Jockey pumping station is unusual, in that calcium and sulphate concentrations are higher than for most groundwater samples at this distance from outcrop (24 km), and sodium concentrations are greater than those for chloride. Although the site is close to the boundary of zones 3 and 4, the groundwater chemistry appears to be influenced by ion exchange rather than mixing with saline water and is therefore more characteristic of

waters from zone 2. As a pumping station, it is possible that fresher water from the west is induced to flow (via fissures) greater distances downdip.

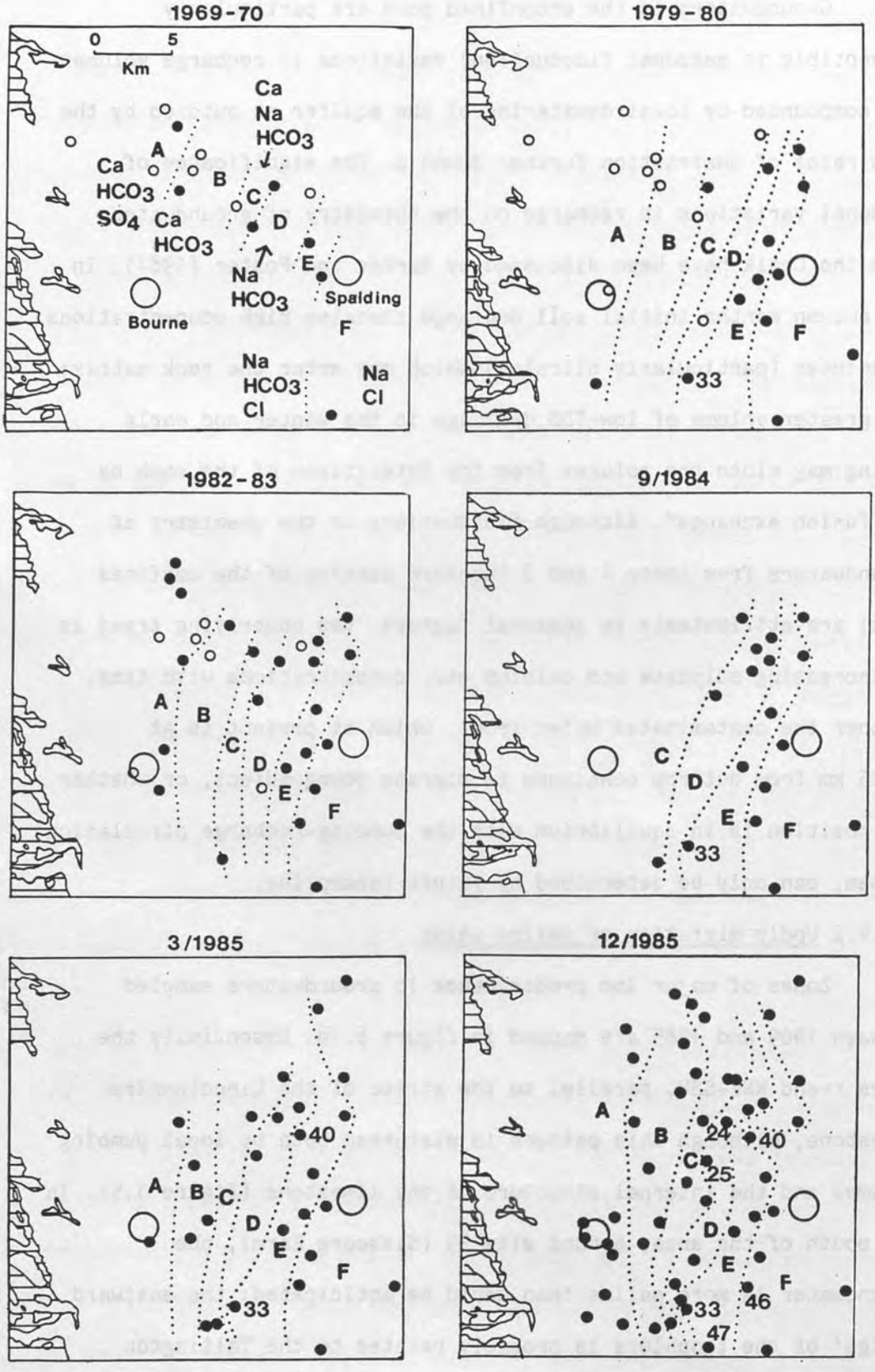
Groundwaters in the unconfined zone are particularly susceptible to seasonal fluctuation; variations in recharge volumes are compounded by local dewatering of the aquifer at outcrop by the high rates of abstraction further downdip. The significance of seasonal variations in recharge on the chemistry of groundwaters from the Chalk have been discussed by Barker and Foster (1981). In the autumn months initial soil drainage contains high concentrations of solutes (particularly nitrates) which may enter the rock matrix; the greater volume of low-TDS drainage in the winter and early spring may elute the solutes from the interstices of the rock by "diffusion exchange". Although fluctuations in the chemistry of groundwaters from zones 1 and 2 (western section of the confined zone) are attributable to seasonal factors, the underlying trend is of increasing sulphate and calcium etc. concentrations with time. Whether the contaminated water front, which at present is at 20-25 km from outcrop continues to migrate downgradient, or whether its position is in equilibrium with the pumping-recharge circulation system, can only be determined by future resampling.

6.3.4.2 Updip migration of saline water

Zones of major ion predominance in groundwaters sampled between 1969 and 1985 are mapped in figure 6.16. Essentially the zones trend NNE-SSW, parallel to the strike of the Lincolnshire Limestone, although this pattern is disturbed both by local pumping regimes and the internal structure of the limestone (figure 1.5). In the south of the area, around site 33 (Sixscore Farm), the groundwater is more saline than would be anticipated; the eastward 'bulge' of the isochlors is probably related to the Tallington

Figure 6.16

Fluctuations in zones of major ion predominance in the groundwaters between 1969 and 1985. Numbered sites are referred to in text.



syncline, the axis of which passes through Deeping St. Nicholas and Langtoft (5.3.2.2).

In March 1985, groundwater of Na-HCO_3 type was obtained at site 40, sodium and chloride determinations were 273 and 238 mg l^{-1} respectively, and an Eh value of +110 mV was obtained. In December the water was twice as saline (Na = 435 and Cl = 436 mg l^{-1}) and more reducing (Eh = -4 mV); the water-type had become Na-HCO_3-Cl. It is unlikely that over-abstraction at the site itself could cause the westward migration of more saline water, as it is used only as an observation borehole. In view of the chemistry of adjacent sites (24 and 25), which even in 1982 were producing Na-HCO_3 type water rather than the Ca-Na-HCO_3 type that would be anticipated from their geographical locations, high abstraction at Jockey pumping station (NGR: 51713265) is a possible cause. Site 24 is a wild borehole, and leakage from other corroded boreholes in the area may also be partially responsible.

Abstraction rates in the east are very low as the water is too saline for agricultural use. Of the easterly sites sampled for this study, only two (46 and 47) are used for domestic supply, the remainder are used as observation boreholes only. In general, the eastern boundary of saline waters at the 200 mg l^{-1} isochlor has remained constant since 1956 (Lamont, 1958), if not earlier. However, general fluctuations in the chemistry of the Na-Cl and Na-HCO_3-Cl waters with time is apparent, as demonstrated in some selected determinations in figure 6.17. The fluctuations could be due to a combination of (1) the precision of the determinations (2) contamination due to the reaction of the water with the borehole casing or (3) seasonal variation. However, the variations in the determinations are greater than that of analytical precision, the boreholes were cleared of standing-water by thorough flushing prior

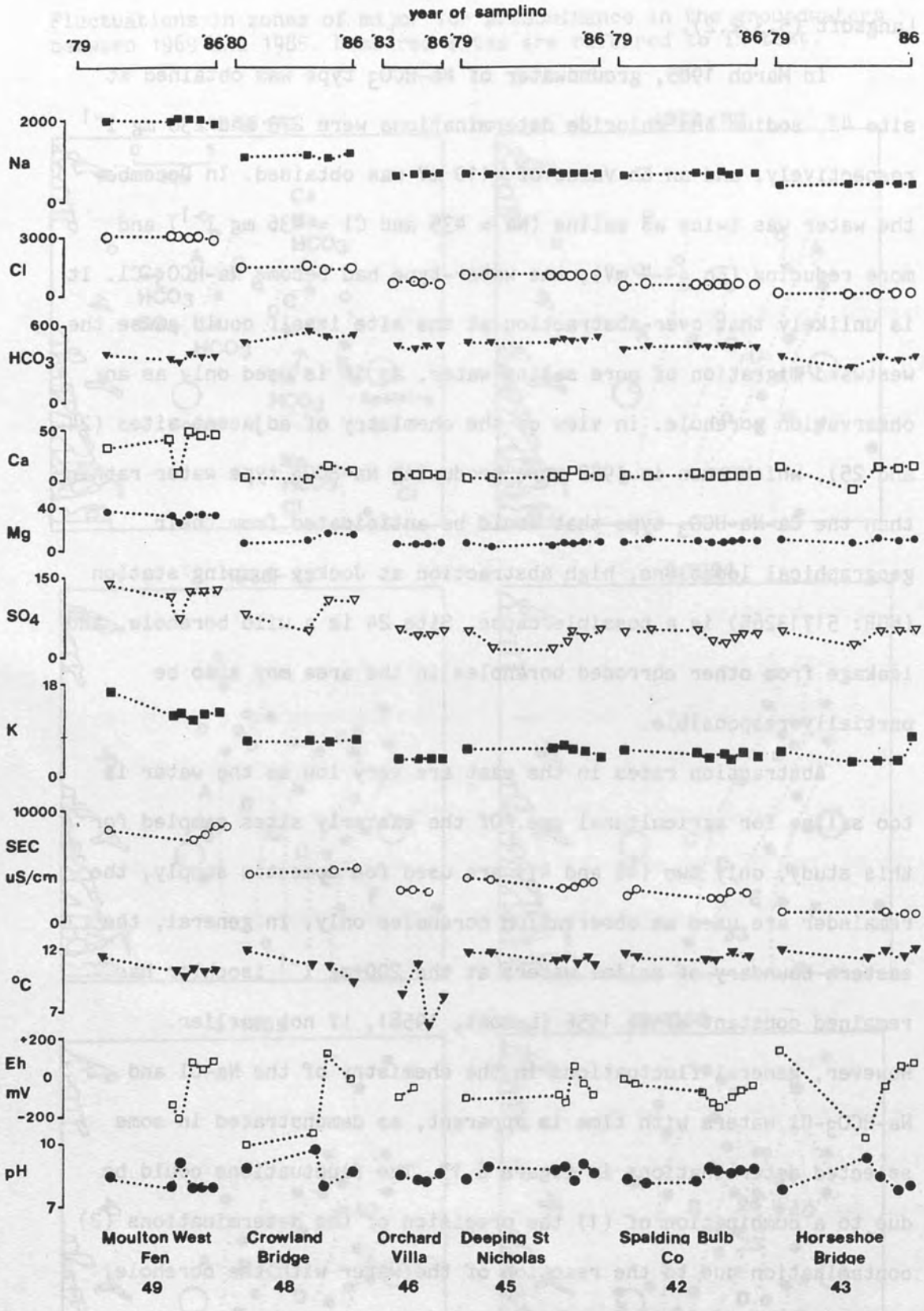

year of sampling
'79
'86
'80
'86
'83
'86
'79
'86
'79
'86
'79
'86
2000
Na
0
3000
Cl
0
600
HCO3
0
50
Ca
0
40
Mg
0
150
SO4
0
18
K
0
10000
SEC
uS/cm
0
12
°C
7
+200
Eh
0
mV
-200
10
pH
7
Moulton West Fen
49
Crowland Bridge
48
Orchard Villa
46
Deeping St Nicholas
45
Spalding Bulb Co
42
Horseshoe Bridge
43

Figure 6.17

Variation in field-determined parameters and major ion concentrations in groundwaters from zones 3 and 4 between 1969 and 1985. Units of concentration: mg l^{-1}

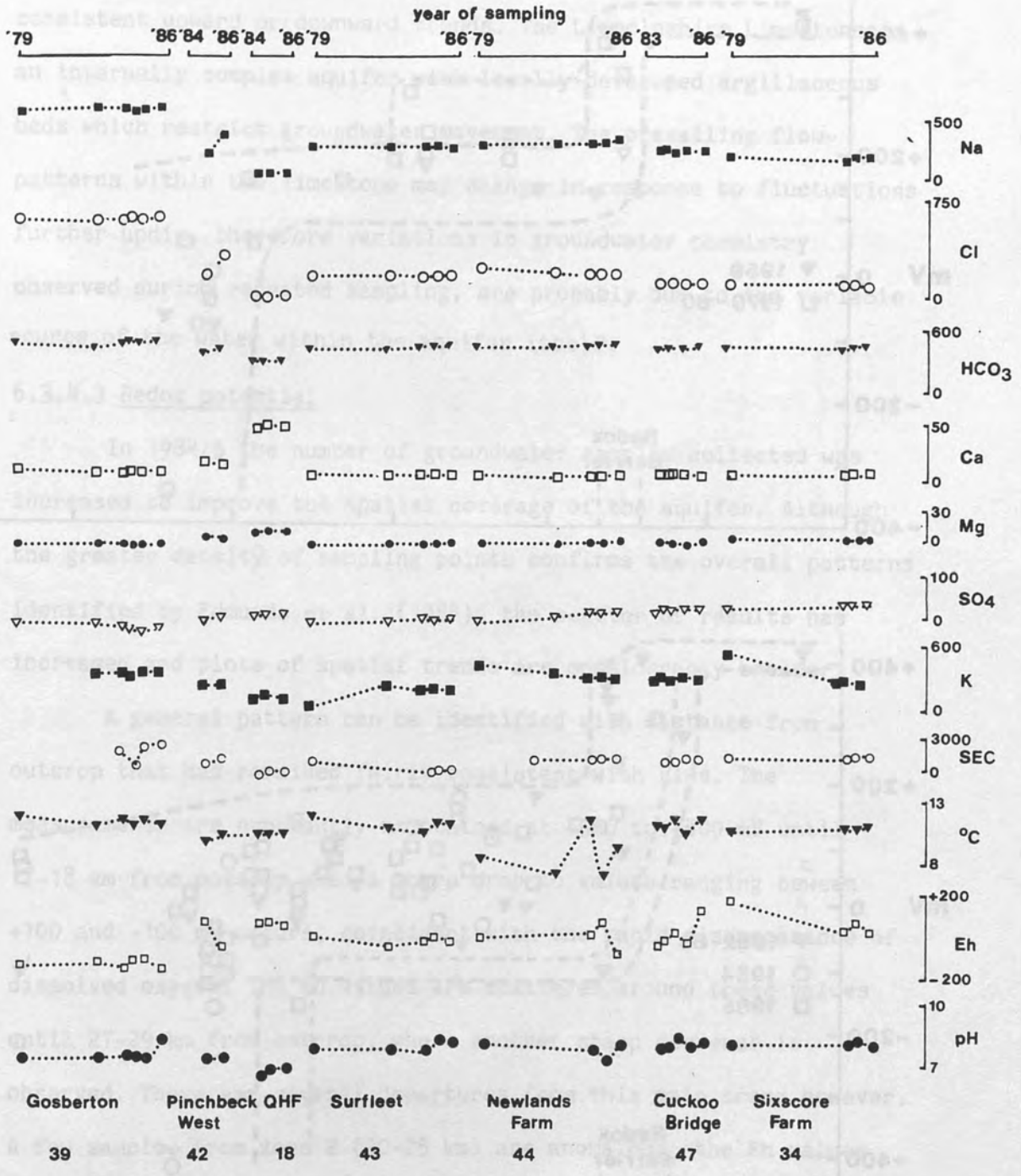
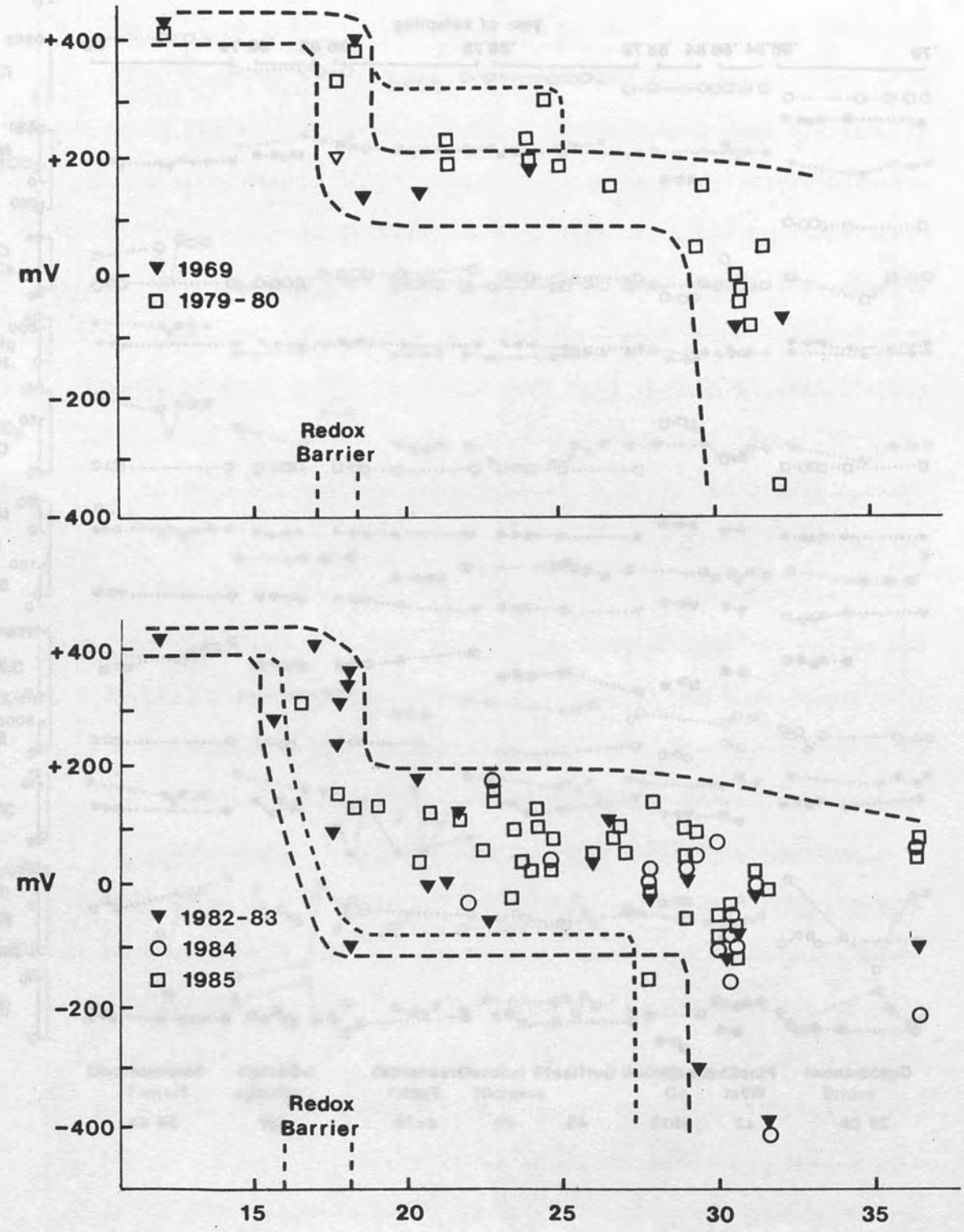


Figure 6.18

Redox potential (Eh) determinations of groundwaters sampled between 1969 and 1985 plotted against distance from outcrop (measured along the transect of figure 5.1).



to sampling and these samples are below the recharge-abstraction circulation system, i.e the volume of the fresh-water influx via fissures at this distance from outcrop would be limited. Bishop (1988) has monitored the groundwater chemistry of several sites over a one-year period and has identified general fluctuations but no consistent upward or downward trends. The Lincolnshire Limestone is an internally complex aquifer with locally-developed argillaceous beds which restrict groundwater movement. The prevailing flow-patterns within the limestone may change in response to fluctuations further updip, therefore variations in groundwater chemistry observed during repeated sampling, are probably due to the variable source of the water within the aquifer itself.

6.3.4.3 Redox potential

In 1984/5 the number of groundwater samples collected was increased to improve the spatial coverage of the aquifer. Although the greater density of sampling points confirms the overall patterns identified by Edmunds *et al.* (1984), the scatter of results has increased and plots of spatial trends are considerably broader.

A general pattern can be identified with distance from outcrop that has remained fairly consistent with time. The measurements are constantly maintained at +350 to +400 mV until 17-18 km from outcrop when a sharp drop to values ranging beween +100 and -100 mV occurs, coincident with the rapid disappearance of dissolved oxygen. The Eh values are scattered around these values until 27-29 km from outcrop, where another sharp decrease is observed. There are several departures from this main trend however. A few samples from zone 2 (20-25 km) are anomalous, the Eh values determined in January 1982 being greater than +200 mV and 30-50 mV higher than repeat measurements obtained in January 1983. The three sites - Jockey pumping station (NGR: 51713265), Rippingale Fen Farm

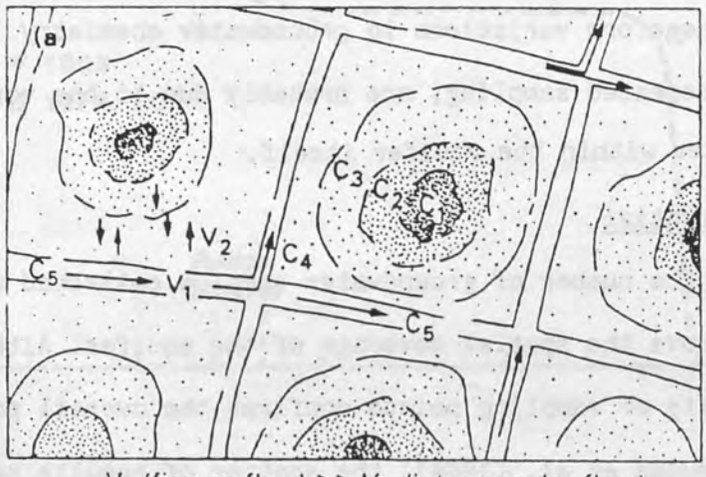
Figure 6.19

Schematic representation of the compositional disequilibrium between interstitial and fissure waters (after Edmunds, 1981).

With reference to the Lincolnshire Limestone:

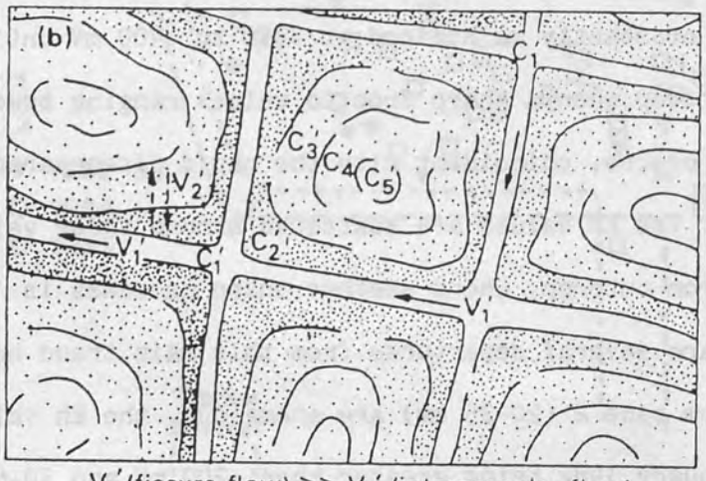
Figure (a) illustrates the displacement of saline interstitial water (C_1') with more recently induced recharge (C_5')

Figure (b) illustrates the dispersion of a pollutant (C_1') with the gradual contamination of interstitial water with initial composition C_5'.



V_1 (fissure flow) >> V_2 (intergranular flow)

$C_1 > C_2 > C_3 > C_4 \geq C_5$



V_1' (fissure flow) >> V_2' (intergranular flow)

$C_1' \geq C_2' > C_3' > C_4' > C_5'$

(NGR: 51483281) and Vicarage Farm (site 22) are within 3 km of each other, therefore it is possible that fresher, oxidised fissure water was obtained by pumping at Jockey pumping station, and that this was abstracted at the other two sites during this sampling period.

Both nitrate (figure 6.14) and oxygen decrease rapidly at the "redox barrier" (6.3.2) to below detectable levels, at which they remain with the exception of a few isolated sites further east. All sets of data indicate that both elements have been consumed by approximately 18 km from outcrop, however there are insufficient sampling points updip to highlight any major temporal trends. The most recent BGS data for the most westerly site at Lenton, are those obtained for 1982; up until that year a small increase in nitrate levels and a slight fluctuation in dissolved oxygen concentrations is recorded. In general, it can be inferred that the redox conditions of the aquifer have changed little since they were first studied in 1969. However, calcium, sulphate and magnesium levels have increased over the same period.

6.4 INTERSTITIAL WATERS

6.4.1 Interstitial waters from the Lincolnshire Limestone core

Interstitial storage within the Lincolnshire Limestone is considerable; however, intergranular flow is of almost total insignificance in comparison with groundwater transport via fissures, flow rates in the unconfined zone of up to 3-7 km/day have been recorded (1.3.1). A compositional disequilibrium therefore exists between recent recharge, rapidly transferred via fissures, and old interstitial water, which migrates through the aquifer matrix by diffusion at probably less than 1 m/year; mixing between the two end-members occurs only when the latter diffuses into fissures (Downing *et al.*, 1977). This situation has been presented schematically by Edmunds (1981), see figure 6.19. The reverse

Table 6.8

Analyses of groundwater and interstitial water samples from Moulton West Fen and Billingborough boreholes. Units of concentration are mg l^{-1}.

	MOULTON WEST FEN		BILLINGBOROUGH		
	Interstitial Water	Groundwater	Interstitial Water		Groundwater
			*Grey	Buff	
Na	2800	1949-2100	18	17	14
K	72	7-12	n.d	n.d	3
Ca	254	32-50	115	340	150
Mg	90	34-39	7	15	7
SO_4	350	117-154	178	1510-3210	141
Cl	3900	2960-3190	50	182-304	32
Si	1.8	2.8-3.2	n.d	n.d	3
Sr	10	4.2-5.3	n.d	n.d	0.3
Li	0.66	0.116-0.129	n.d	n.d	0.005
F	2.3	1.8-2.1	n.d	n.d	0.13
Br	12.2	11-16	n.d	n.d	0.15

Interstitial waters were obtained by centrifugation of the rock core by BGS. *Both grey and buff coloured limestone samples from Billingbrough borehole were spun.

Groundwater samples have been collected from Moulton West Fen borehole since 1980, the range of groundwater concentrations obtained between 1980 and 1985 are presented.

situation, as exemplified by the influx of agrichemicals (e.g. calcium, sulphate and nitrate ions) into the confined zone, is represented by the second diagram.

Interstitial water obtained by the centrifugation of Lincolnshire Limestone rock core has been analysed by BGS. The samples were from boreholes near Billingborough and at Moulton West Fen (site 49) and therefore represent waters from zones 1 and 4, respectively. Analyses of the porewater and groundwater from these sites are presented in table 6.8.

At Billingborough, the order of increasing abundance of major ions in the porewater is the same as that in the bulk groundwater sample (i.e. the "fissure water"):

$$Mg < Na < Cl < Ca < SO_4$$

However, the latter is not a simple dilution of the water trapped in the interstices of the rock, the ratios of the ions in the two solutions are very variable. For example, the sulphate content of the bulk groundwater sample is only one-fifth of that in the interstitial water, while sodium in the fissure waters appears to have attained equilibrium with that in the pores. The ratios of the ions in the fissure water, relative to the porewater increases in the order:

$$SO_4 < Cl < Ca < Mg < Na$$

and are plotted schematically in figure 6.20.

The porewater chemistry of core from Moulton West Fen is more saline than the bulk groundwater sample; the ratio of the porewater to seawater for sodium, chloride, bromide and conductivity being 0.20 ± 0.03, and for the groundwater 0.17 ± 0.01. As with the water samples from Billingborough, the order of increasing abundance of ions in the fissure water reflects that of the interstitial water:

$$Li < Sr < Br < K < Mg < Ca < SO_4 < Na < Cl$$

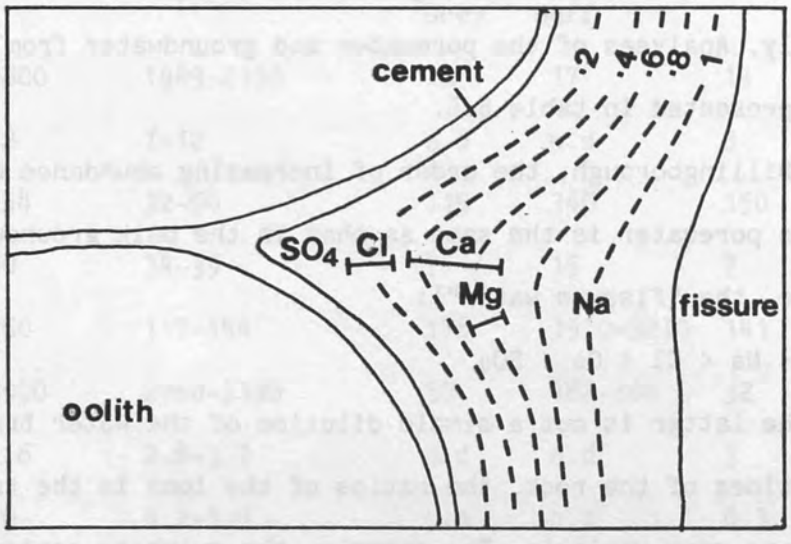
Figure 6.20

A schematic representation of the ratios of major and minor ion concentrations in interstitial waters with respect to those of groundwater samples, from Billingborough and Moulton West Fen boreholes.

BILLINGBOROUGH

Decreasing order of absolute concentrations of ions in the two water samples:

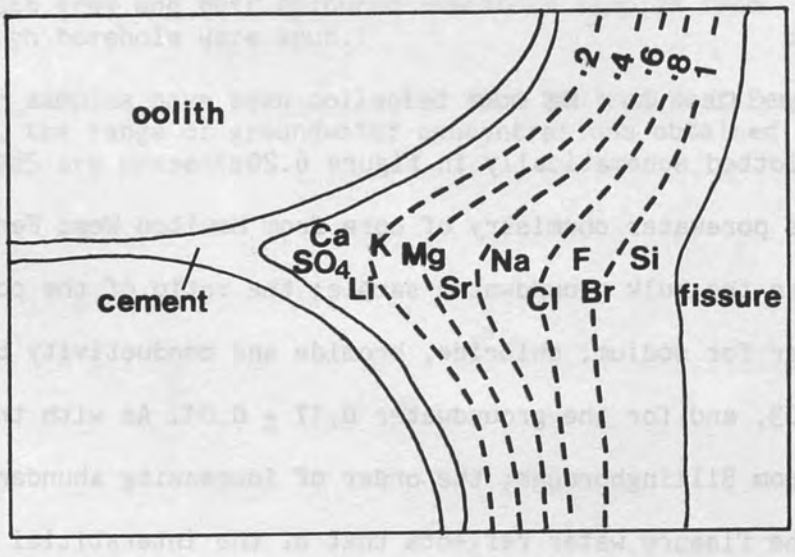
SO_4 > Cl > Ca > Na > Mg



MOULTON WEST FEN

Decreasing order of absolute concentrations of ions in the samples:

Cl > Na > SO_4 > Ca > Mg > K > Br > Sr > F > Si > Li



and the ratios between the the analyses vary, increasing in the following order:

SO_4 < Ca < Li < K < Mg < Sr < Na < Cl < F < Br

(figure 6.20). As before, only one-fifth of the sulphate held in the interstices has been released into the bulk groundwater, while bromide appears to have equilibrated in the solutions; silicon is more abundant in the groundwater. At this site the concentrations of sodium, chloride and bromide in both waters exceed those in the rock itself.

In zone 1, the major ion concentration of the groundwaters is controlled by incongruent dissolution of the carbonate matrix, the influx of agrichemicals and minor gypsum dissolution. Sodium and chloride levels in rainfall are low; chloride derived from overlying argillaceous deposits and from road-salt may enter the aquifer with surface run-off at outcrop and be enhanced by evaporation; sodium tends to be removed by adsorption during infiltration of the water through the soil zone. Thus calcium and sulphate concentrations in the Billingborough sample are an order of magnitude greater than those of sodium and chloride.

The groundwater close to outcrop is highly oxygenated (12 mg l^{-1} at Lenton borehole) as indicated by the proportion of buff, oxidised limestone either side of the fissures, to the residual lenses of unaltered, grey limestone. The proportions of buff to grey limestone have been estimated by Lawrence and Foster (1986). At outcrop, buff limestone accounts for about 50% of the core, decreasing to approximately 5%, 5 km west of the redox barrier, and 2% at the barrier itself, where oxygen and nitrate levels fall below the detection limit. The analyses of buff and grey limestone core reveal no consistent trends (5.2.2), some geochemical fluctuations being at or below the levels of precision of the determinations.

However sulphate, calcium, chloride and magnesium levels are markedly lower in interstitial waters from the buff limestone in comparison with waters from the grey, reduced core. Sodium levels are unaffected. Thus the limestone either side of fissures would appear to be areas of active carbonate/gypsum dissolution and iron sulphide/hydroxide oxidation etc., the liberated elements being rapidly removed and dispersed throughout the aquifer.

High rates of abstraction in zones 1 and 2 have resulted in a reversal of the hydraulic gradient further down-dip. As the diluting influence of fresh fissure-water diminishes, the saline interstitial component of the groundwaters in the east increases, signalled by an increase in the concentrations of the halides, alkali and alkali earth elements. By zone 4, over half of the calcium has been exchanged for sodium and oversaturation with respect to all the carbonate minerals limits its release to gypsum dissolution. Being so far from outcrop, the older interstitial component of the groundwater from Moulton West Fen borehole is dominant, the sodium and chloride concentrations are therefore one or two orders of magnitude greater than those of calcium and sulphate.

Elsewhere in the Lincolnshire Limestone chloride levels approach that of seawater. At Woodhall Spa (NGR 51953636) for example, a chloride concentration of 13500 mg l^{-1} has been recorded (Downing and Williams, 1969).

6.4.2 Source of the saline water

The saline interstitial waters have often been assumed to contain a connate component (Downing and Williams, 1969; Edmunds, 1973) and this hypothesis appeared to be confirmed by Andrews and Lee's (1980) helium isotope results. However, other isotope data have yielded considerably younger ages, and the practice of extrapolating a groundwater ^{4}He age of 4 million years to 170

million years, on the basis of chlorinity, is probably untenable; Downing *et al.* (1977) for example, found no consistent correlation between chlorinity and age. Oxygen, hydrogen and carbon isotope data from the latter study, revealed a meteoric origin for the waters, with a maximum age of 25000 years. Rainfall on the Lincolnshire Limestone outcrop during the Pleistocene was cited as the most plausible source.

The groundwaters collected in March 1985, were found to have an $^{87/86}Sr$ ratio similar to that of modern seawater, with a maximum extrapolated age of 6 million years (Smalley *et al.*, in press). It was initially thought that the saline groundwaters were attributable to the modification, by dilution and/or calcite and halite precipitation, of seawater which had either migrated updip or had flooded the outcrop, possibly during the Pliocene. The Lincolnshire Limestone grades into a siltier facies downdip, which outcrops on the floor of the North Sea, east of the Sole Pit Trough (G. Lott, *pers. comm.*, 1985); however, alternative isotope data and the major ion chemistry (see the Piper diagram, figure 5.6) preclude modern seawater intrusion of the aquifer as the source of the saline water. The flooding of the limestone outcrop by Pliocene seawater is inconsistent with the diagenetic regime of the formation and with the continual uplift and eventual exposure of the Limestone throughout the Tertiary (Emery, 1986; Emery *et al.*, 1987). Analyses of the same groundwater samples for oxygen and hydrogen isotopes have since confirmed the meteoric origin proposed by Downing *et al.* (1977), Smalley *et al.*, (1986).

The $^{87/86}Sr$ ratio of two burial cement phases in the limestone is considerably higher than that of Bajocian marine carbonate phases (Emery *et al.*, 1987). Two possible sources of the radiogenic strontium are: (1) detrital material - clays, micas and

potassium feldspars - associated with the argillaceous strata within and confining the aquifer (2) remobilized Palaeozoic marine carbonate and/or sulphate (e.g. from the Carboniferous Limestone). Homogenisation of meteoric waters in contact with both carbonate phases and with the detrital material itself could yield groundwaters with the high $^{87/86}Sr$ ratios (Emery *pers. comm.*, 1988). Strontium isotope ratios are therefore unsuitable for use in identifying the origin of the saline waters of the Lincolnshire Limestone. However, they have been useful as a natural tracer in the semi-quantitative modelling of the mixing process between the saline interstitial waters and fresher recharge. The strontium isotope data also reveal that post-depositional cross-formational flow must have occurred to produce the $^{87/86}Sr$ signature of the burial cements in the aquifer matrix.

The most likely mechanism for the concentration of the meteoric waters, to the saline waters encountered at depth in the aquifer, is membrane-filtration, as envisaged for the formation of oil-field brines. Under hydraulic pressure the water is forced upwards; when intercalated clay beds are encountered the excess negative charge of the clays repel anions, hindering their upward migration; cations are also retained to maintain electrical and chemical neutrality. Shaley horizons may therefore act as semi-permeable membranes: water molecules pass through them, but the filtrate has a lower salt content than the original solution (Bredehoeft *et al.*, 1963; Collins, 1975; Matthess, 1982).

The Lincolnshire Limestone contains several argillaceous units, notably the Clipsham Member (uppermost unit) and Scottlesthorpe Beds (Middle Lincolnshire Limestone); a predominantly clastic unit, the Upper Estuarine Series confines the aquifer from above. It is plausible therefore, that the groundwaters below the

Table 6.9

Summary of major processes controlling the spatial behavior of major and minor ions in groundwaters from the southern Lincolnshire Limestone

	ZONE 1	ZONE 2	ZONE 3	ZONE 4
Dominant ions	Ca, HCO_3, SO_4	Ca, HCO_3	Na, Ca, HCO_3	Na, Cl
Criterion for demarcation of western zone boundaries	Start of unconfined zone	Initial Na increase at expense of Ca	Initial Cl increase	Cl > 200 mg l^{-1} (advised limit for public supply)
Dominant processes/ features	Incongruent calcite dissolution (redox barrier)	$Ca \rightleftharpoons 2Na$ ion exchange	increasing proportion of saline interstitial water as influx of fresh recharge water from W diminishes	
Ions/parameters at maximum concentrations	O_2, NO_3, Eh		Mg, Sr, Ba	Groups I, II
	Ca, SO_4, V		Si, F	and VII, HCO_3,
	<- Fe ->			S, P, B,
	<- Mn ->			T, pH

general recharge-abstraction circulation system are concentrated by a combination of membrane-filtration and continual leaching as the residence time of the interstitial waters increases. Ion exchange, sulphate-reduction, mineral precipitation and diffusion from adjacent beds are probably also important processes in the modification of the saline waters at depth.

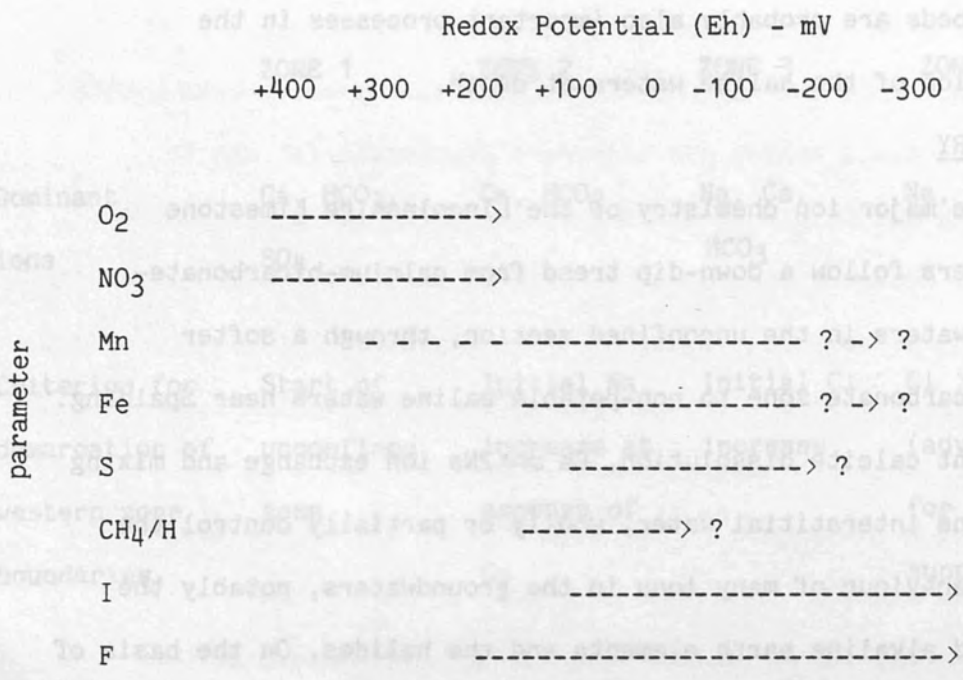
6.5 SUMMARY

The major ion chemistry of the Lincolnshire Limestone groundwaters follow a down-dip trend from calcium-bicarbonate-sulphate waters in the unconfined section, through a softer sodium-bicarbonate zone to non-potable saline waters near Spalding. Incongruent calcite dissolution, $Ca \rightleftharpoons 2Na$ ion exchange and mixing with saline interstitial water, wholly or partially control the spatial behaviour of many ions in the groundwaters, notably the alkali and alkaline earth elements and the halides. On the basis of these processes the sampling area has been divided into four zones (table 6.9). The boundary of zones 3 and 4 is delineated by the 200 mg l^{-1} isochlor, the advised limit for potable public supply.

Fissures in the limestone form conduits for the transfer of fresh aerated recharge down the hydraulic gradient. Oxidation of the organic matter and iron sulphides in the fissure walls produces buff-coloured zones, which decrease in proportion to the grey residual limestone with distance from outcrop. By approximately 17 km along the line of section, the dissolved oxygen has been completely consumed, the oxidised, buff limestone portion is minimal, and the field Eh values for the groundwaters drop from +300-+350 mV to +50-+150 mV. This "redox-barrier" is coincident with the complete removal of nitrates by bacterial reduction. Once reducing conditions prevail, ferrous iron, manganese, sulphide, iodine and fluoride are released into solution. Redox potentials can

Figure 6.21

Summary of approximate redox zones for ions in the Lincolnshire Limestone groundwaters



An oily odour thought to be methane and/or hydrogen was detected in groundwater samples with field Eh values of approximately +150 to -50 mV; however, Bishop (1988) has determined methane in waters at depth with lower redox potentials.

only be interpreted semi-quantitatively, nevertheless, the release of these ions is limited to specific ranges of Eh values (figure 6.21), although the lack of Eh determinations in the -150 to -300 mV range precludes the demarcation of the lower limit of the redox zones. Oxygen and nitrates are removed at the redox barrier where a sharp drop of 200 to 300 mV in Eh values occurs. Iron release is controlled by the precipitation of ferric hydroxide in the oxidising waters and by sulphides at depth; manganese and fluoride release is concomitant with iron reduction and iodine is released from organic matter once the Eh has dropped below 0 mV, coincident with the main liberation of sulphide.

Most of the trace metals determined in the groundwaters (Ti, Zr, V, Nb, Co, Ni, Mo, Cr, Cd and Pb), occur at concentrations below the limits of detection (0.5 -1 $\mu g\ l^{-1}$), although V, Cu and Zn were detectable at some sites. The low levels are maintained by a combination of low geochemical abundance, solubility controls, complex-formation, pH and adsorption. The solubilities of Co, Ni, Pb and Cu carbonates and sulphides are significant, while adsorption on clay minerals, organic matter and colloids limit the release of the alkali, alkaline earth elements, phosphorus and possibly boron, in addition to many of the heavy metals. Aluminium release from clay minerals etc., is primarily restricted by the alkalinity, since kaolinite hydrolysis requires a pH <5.

Rare earth elements are present at very low concentrations (La = <0.1-1 $\mu g\ l^{-1}$). The shale normalised signature of the groundwaters is the reverse of that of the Upper Estuarine Series samples and the basal and uppermost beds of the Lincolnshire Limestone. The groundwater demonstrate relative light REE depletion, due to the greater adsorbability of the light REEs and the higher solubilities of the heavier elements.

CHAPTER SEVEN

7. THE HYDROGEOCHEMISTRY OF THE SOUTHERN LINCOLNSHIRE LIMESTONE: A SUMMARY

7.1 CONTEXT OF STUDY

The Lincolnshire Limestone is one of the most well-studied aquifers in the U.K. Geological research commenced in the nineteenth century, however more recent investigations have included the revision of the stratigraphy of the aquifer (Ashton, 1980) and studies of diagenetic processes (Emery, 1986), carbon and strontium isotope signatures of the rocks and waters (Emery *et al.*, 1987; Bishop, 1988), redox processes in the groundwaters (Edmunds *et al.*, 1984) and the problem of nitrate pollution (Lawrence and Foster, 1986).

The dominant hydrochemical trends and processes of the southern Lincolnshire Limestone identified by the earlier studies have been confirmed using ICP-OES as the primary analytical technique. The number of trace element determinations has been extended to include the rare earth elements and dissolved sulphide. By collecting groundwaters on four sampling trips over two years, short-term hydrochemical fluctuations can be compared with the longer-term trends identified by earlier research.

In addition to the groundwater analyses, samples of rock core from the Lincolnshire Limestone and overlying lithologies have been analysed using ICP-OES, enabling geochemical constraints on the minor and trace element distributions in the groundwaters to be better understood.

7.2 GEOLOGY AND HYDROGEOLOGY

The Lincolnshire Limestone is a predominantly oolitic formation of the Middle Jurassic (Bajocian) in eastern England. The aquifer is between 10 and 30 m thick and structurally simple on a

regional scale with an easterly dip of one degree. From the internal structure and facies relationships it is thought to represent the landward migration of an off-shore barrier across lagoonal and tidal mud-flat deposits. The aquifer is confined by predominantly clastic sequences, the Grantham Formation (formerly Lower Estuarine Series) below, and the Upper Estuarine Series above.

The aquifer is recharged at outcrop via swallow holes, losing streams and through the soil zone. Groundwater flow down-gradient is primarily via the extensive fissure network, with flow-rates of several km/day recorded in the unconfined zone. Interstitial flow through the aquifer is negligible. In the confined zone, high rates of abstraction from public supply pumping stations have caused local reversals in the direction of groundwater flow, thus, by 20-25 km from outcrop the eastward influx of fresh recharge water is minimal.

7.3 GEOCHEMISTRY

Lithologically and geochemically the aquifer is very heterogeneous, with carbonate-cemented oolites (90-95% $CaCO_3$) intercalated with argillaceous limestones. In comparison with the oolitic samples the latter are relatively enriched in Fe, Mg, K, Na, Ti, Sr, Ba and Y and contain 26-35% calcium (by weight), up to one-quarter of which occurs as gypsum.

The total determined REE (La, Ce, Nd, Sm, Dy, Ho, Er, Yb and Lu) + Y concentrations for the oolitic samples are in the 10-30 mg kg^{-1} range; most of the argillaceous limestones contain up to 100 mg kg^{-1}. The lanthanum concentrations of the oolitic and argillaceous limestones, are 0.06-0.1 and 0.1-0.5 times those of a standard shale respectively, and the shale-normalised signatures of both sets of samples are flat.

The argillaceous limestones at the very top (Clipsham Member) and base of the Lincolnshire Limestone have REE

concentrations and shale-normalised signatures similar to those of the overlying Upper Estuarine Series: the maximum ΣREE + Y concentrations are approximately 1000 mg kg^{-1}, with lanthanum concentrations up to five times that of a standard shale. Although the shale-normalised plots of the upper and basal argillaceous limestone samples reveal heavy REE depletion, due to the greater adsorbability of the light REEs and greater solubility of the heavier elements, the argillaceous and oolitic limestone samples from the main body of the aquifer have a flat, shale-normalised plot, indicative of dilution of the terrigenous input without fractionation.

In comparison to all the Lincolnshire Limestone samples, the overlying Upper Estuarine Series is relatively enriched in Si, Al, V, Mo, Nb, Sc, Y, Zn and the REEs, being enriched in La relative to a standard shale by a factor of six.

7.4 HYDROCHEMICAL PROCESSES AND GEOCHEMICAL LIMITATIONS

The groundwaters of the Lincolnshire Limestone follow a trend down-gradient from calcium, bicarbonate and sulphate-dominated waters in the unconfined zone, through a softer sodium bicarbonate type water to sodium and chloride-dominated waters in the east. The major and minor element chemistry is controlled primarily by the processes of incongruent calcite dissolution (zone 1), $Ca \rightleftharpoons 2Na$ ion exchange (zone 2) and mixing between fresh recharge waters transported by fissures and older saline, interstitial water (zone 3). The proportion of interstitial waters increases with distance from outcrop. Chloride levels exceed the limit of potable water for public supply (200 mg l^{-1}) a few km west of Spalding, increasing to 750 mg l^{-1} at Spalding and 3000 mg l^{-1} a further 5 km to the east.

Incongruent calcite dissolution releases magnesium and strontium from the carbonate lattice into the waters until competing

processes (ion exchange and adsorption) increase in importance. Ion exchange facilitates the increase of sodium concentrations at the expense of calcium and the remaining alkali, alkaline earth elements and halides increase due to the mixing process.

The occurrence and mobility of many minor and trace elements in the groundwaters are controlled by the Eh-pH conditions of the aquifer and limited by the quantities available for leaching in the aquifer matrix itself.

Reduction-oxidation reactions control the behaviour of O, N, Fe, Mn, S, F and I. Oxygen and nitrates are removed at the redox barrier, where a sharp drop of 200 to 300 mV in Eh values occurs. Ferric and manganese oxides and hydroxides maintain low concentrations of iron and manganese in the oxidising zone; heavy metals and possibly fluoride, may be adsorbed onto the precipitates. With the onset of mildly reducing conditions (<+200 mV) ferrous iron, manganese and fluoride are released into solution. As the redox potential drops another 50 mV, sulphide release commences and an oily (rather than sulphide) odour is detected at the well-head, thought to indicate methanogenesis and/or hydrogen liberation. Once the Eh has fallen below 0 mV, iodine is released from organic matter in the limestone and sulphide liberation accelerates. Iron concentrations also decrease, probably due to the formation of the monosulphide as amorphous FeS precipitate and/or mackinawite. Manganese levels in the uncontaminated groundwaters are highly correlated with iron concentrations throughout the aquifer; at depth the concentrations decrease, the lower redox boundaries for both elements being between -150 and -250 mV. Once iron and manganese levels decrease, fluorite solubility controls and/or aluminium complex-formation may take over as controls on fluoride release.

The base level concentrations of most heavy metals in the

groundwaters are below detection limit levels (usually <0.5-1 $\mu g\ l^{-1}$), with the exceptions of iron, manganese and zinc, which have median concentrations in the uncontaminated groundwaters of 194, 3.1 and 16.5 $\mu g\ l^{-1}$, respectively.

Adsorption mechanisms, complex formation, and solubility controls limit the occurrence and mobility of many minor and trace elements within the groundwaters. The low solubilities of the carbonates and/or sulphides of Ba, Co, Ni, Zn and Pb, and of Ti, V, Cr, Cu, Cd, As, Al, Sc and REE complexes, are probably of great importance in the prevailing Eh-pH conditions of the aquifer. Adsorption onto clay minerals, organic matter, iron and manganese hydroxides etc., probably limit the release of Ba, K, Cs, Rb, Nb, Co, Ni, Mo, Cr, Zn, Pb, As, $H_2PO_4^-$ and possibly $H_3BO_{3(aq)}$ into solution. Ultimately however, groundwater concentrations of the trace metals are limited by their very low abundance in the limestone. The oolitic beds are very pure, heavy metals tending to be relatively concentrated in the intercalated marl and shaley beds. Median concentrations of the metals in the limestone in order of increasing concentration ($mg\ kg^{-1}$) are: Zn (<5), Mo (<9), Sc (6), Cr (12), Co and Nb (16), V (28), Ni (43), Zr (67), Mn (187), Ti (620) and Fe (5443). A contribution from the confining lithologies is also likely, particularly where they are in hydraulic continuity with the aquifer.

The rare earth elements are associated primarily with the argillaceous beds within the aquifer and the confining formations, most samples within the main body of the Lincolnshire Limestone contain 0.05-1 times the REE abundances of a standard shale. The groundwater REE concentrations are five or six orders of magnitude less than that of a shale, with lanthanum concentrations in the <0.05 to 1 $\mu g\ l^{-1}$ range. A strong light REE depletion was apparent

in the partial analyses of six groundwaters, the reverse of the shale-normalised signatures of the top and basal argillaceous limestones and Upper Estuarine Series, reflecting the higher solubilities of the heavy REE complexes and the greater adsorbability of the light REEs. Although the groundwater samples analysed are reducing (<+50 mV), they are alkaline enough for the oxidation of cerium to Ce^{4+} to occur. Its precipitation and therefore depletion relative to other light REEs would be anticipated, however the results are inconclusive in this respect.

7.5 SALINE GROUNDWATER AND INTERSTITIAL WATERS

In central Lincolnshire groundwater chloride concentrations from the aquifer have been known to approach that of seawater. In southern Lincolnshire where different fluid-flow patterns prevail due to the lower regional dip of the aquifer and the more extensive fissure network, far less saline waters have been encountered. Samples taken from around Spalding suggest that the proportion of sodium and chloride ions continues to increase with distance from outcrop, however, groundwater samples from Moulton West Fen borehole (37 km from outcrop) reveal that unless waters from this site are anomalous, the trend does not continue further east in southern Lincolnshire.

The source of the saline water at depth has been the subject of some debate. It is unlikely that a connate component still remains, and carbon, oxygen and hydrogen isotope analyses of the groundwaters reveal a meteoric origin. It is thought that the waters originated as rainfall during the Pleistocene and that they have inherited their high TDS content by a combination of prolonged rock-water contact and membrane-filtration mechanisms.

In order to further develop current theories on the formation of the saline waters, definition of the saline end-member in

southern Lincolnshire is necessary.

7.6 SEASONAL AND ANTHROPOGENIC INFLUENCES

Seasonal lowering of the water-table at outcrop allows the direct infiltration of surface run-off from losing streams etc., into the aquifer. Overabstraction in the past, from zones 1 and 2, has exacerbated the problem. As the Lincolnshire Limestone outcrop, is extensively farmed, an increase in fertiliser-derived ions has occurred. Calcium, sulphate and magnesium concentrations in zone 1, have increased by an average of 10% since 1969, although this phenomenon has also been observed in groundwaters from a pumping station at the boundary of zones 2 and 3, which marks the western limit of the main zone of abstraction.

The increase in the concentrations of other contaminants e.g. potassium, chloride and nitrate, is less marked. Nitrate levels in potable groundwaters are currently the source of considerable public concern, and further north many samples exceed the advised EEC limit for public potable supply (40 mg l^{-1} NO_3-N). In southern Lincolnshire, fluctuations in the nitrate levels in the unconfined zone are apparent. However, their encroachment into the confined zone has been limited. Since 1969 the redox-system has changed very little: the redox-barrier has remained a distinct phenomenon and its location unchanged, thus the decrease in nitrate levels below the 0.4 mg l^{-1} NO_3-N detection limit still occurs 1-3 km downdip of the onset of confined conditions. Careful monitoring of the nitrate concentrations in the groundwaters and a reduction in the quantities entering the unconfined zone are required to safeguard the supply of nitrate-free waters in the confined zone, with which contaminated waters may be diluted.

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APPENDICES

APPENDIX 1

DEFINITIONS OF HYDROLOGICAL TERMS REFERRED TO IN SECTION 1.3.

POROSITY (%)

$a = V_p / V_b \times 100$ where: V_p = volume of voids
V_b = bulk volume of rock

PERMEABILITY (darcys)

1 darcy = the permeability that permits a flow of 1 ml of fluid of 1 centipoise viscosity completely filling the pores of the medium to flow in 1 second through a cross-sectional area of 1 cm^2 under a gradient of 1 atmosphere/cm of flow path.

HYDRAULIC CONDUCTIVITY (e.g. m/day)

The relationship between intrisic permeability (K) and hydraulic conductivity (k) or field permeabilty is
$k = Kv/g = K\mu/\rho g$
where: v = fluid kinematic viscosity
μ = dynamic viscosity
ρ = density
g = gravitational acceleration

TRANSMISSIVITY (e.g. m^2/day)

$T = kb$ where: k = hydraulic conductivity
b = aquifer thickness

STORAGE COEFFICIENT

The volume of water released from storage per unit surface area of the aquifer for each unit change of head.
In unconfined conditions, the storage coefficient is usually equivalent to the specific yield.

APPENDIX 2

GROUNDWATER ANALYSES USING NON-ROUTINE ICP-OES TECHNIQUES

Table 2.1A Lincolnshire Limestone groundwater analysis by ICP-OES: A comparison of two preconcentration methods

Table 2.2A REE and Y in the groundwaters

Table 2.3A Comparison of Philips and ARL ICP-OES groundwater analyses

A comparison of two preconcentration methods **Table 2.1A**

Notes

* ARL: ICP-OES analysis of water samples on the ARL 34000C instrument at Wallingford (see 3.4)

+ P: The water samples were completely evaporated to a residue (see 4.3), and analysis of the solutions of residue digests performed using the Philips PV4890 instrument. The Na, K, Ca, Mg, Si, Fe, Mn, Ti and Al concentrations were converted from weight % oxide data and the trace elements from ppm to mg l^{-1} and µg l^{-1}. LQDCs are presented in table 3.5A

SAMPLE SET A (collected March 1985)
ARL - direct measurement of groundwaters without preconcentration
P - waters were evaporated to a residue in geochemistry lab; sample preparation and analysis was carried out at King's

SAMPLE SET B (collected December 1985)
ARL - the samples were preconcentrated 20 times by evaporation
P - evaporation to residue was carried out under clean room conditions at Wallingford, sample preparation and analysis at RHBNC

I.B: The ion balance was calculated from Na, K, Ca, Mg and SO_4 determinations from each analysis with Cl and HCO_3 data (3.5).

Total mineralisation was calculated from the complete water analysis (including major anions) in mg l^{-1}.

C.F: Concentration factors for those elements determined in the "trace element solutions" (i.e. not Si and Na).

Sulphate is determined routinely by the ARL system.
The determination of sulphate in the residue solutions was performed using the Philips ICP source in conjunction with a vacuum monochromator (see 4.4)

Cadmium, rubidium and lead were determined in the residue digests by AAS (see 3.3)

Table 2.1A

A comparison of two preconcentration methods - sample set A

	CHEAL BRIDGE		SURFLEET		SIXSCORE FM		HORSE. BR.	
	* ARL	+ P	ARL	P	ARL	P	ARL	P
	mg l^{-1}		mg l^{-1}		mg l^{-1}		mg l^{-1}	
Na	167	n.d	322	n.d	286	256	270	369
K	2.6	1.5	2.7	1.5	2.7	1.5	2.8	1.6
Ca	20	14	5	4	7	6	16	9
Mg	14.2	10.0	3.6	3.1	5.8	4.5	6.9	4.6
Si	3.9	n.d	3.7	n.d	3.6	3.9	3.3	<3
Sr	1.49	1.07	0.41	0.40	0.68	0.55	0.77	0.41
SO_4	26	26	18	16	38	39	31	21
	µg l^{-1}		µg l^{-1}		µg l^{-1}		µg l^{-1}	
Fe	105	<70	45	<61	37	<53	29	<54
Mn	<3	<77	<3	<135	<3	<117	<3	<121
Ti	n.d	<155	n.d	<255	n.d	<227	n.d	<240
Al	<100	<79	<100	<46	<100	40.2	<100	<42
Rb	n.d	<2.5	n.d	<3.5	n.d	<3.8	n.d	<3.9
Cd	<25	<0.2	<25	<0.4	<25	n.d	<25	<0.3
Pb	<200	<5	<200	<9	<200	n.d	<200	<8
		±1		±1.6		±1.5		±1.6
Ba	13	11	4	6.1	8	7.6	9	6.8
Co	<20	2	<20	<1.6	<20	1.5	<20	1.6
La	<20	3	<20	<1.6	<20	1.5	<20	2.3
Li	16	15	18	17	18	18.2	19	15.6
Nb	n.d	1.5	n.d	<1.6	n.d	1.5	n.d	1.6
Ni	<100	1.5	<100	<1.6	<100	<1.5	<100	<1.6
Sc	<2	<1	<2	<1.6	<2	<1.5	<2	<1.6
V	<20	1.5	<20	<1.6	<20	<1.5	<20	<1.6
Y	<2	<1	<2	<1.6	<2	<1.5	<2	<1.6
Zr	<15	<1	<15	<1.6	<15	<1.5	<15	<1.6
		±2.5		±4.3		±3.8		±3.9
Cr	<30	24	<30	13	<30	13.7	<30	18.7
Cu	<10	6	<10	<4.3	<10	<3.8	<10	<3.9
Zn	<20	5.5	<20	<4.3	<20	12.9	<20	<3.9
		±4.5		±7.8		±6.8		±7.0
Ce	n.d	6	n.d	<7.8	n.d	<6.8	n.d	<7.0
Mo	<100	4.5	<100	<7.8	<100	<6.8	<100	<7.0
I.B	1.8%	-	0.6%	-	0.6%	4.3%	2.5%	15%
T_{min}	693		1075		971		938	
C.F	0	193	0	117	0	131	0	125

Table 2.1A

Sample Set A continued

	CUCKOO BR.		DONINGTON		GOSBERTON	
	ARL	P	ARL	P	ARL	
	mg l^{-1}		mg l^{-1}		mg l^{-1}	
Na	292	342	444	321	673	n.d
K	2.7	2.0	3.1	1.8	4.3	2.3
Ca	7	7	9	7	8	8
Mg	3.4	3.5	6.7	5.4	6.7	5.4
Si	3.6	<4	2.8	<5	3.4	n.d
Sr	0.38	0.39	0.81	0.66	0.83	0.67
SO_4	31	43	<0.5	1	0.5	2
	µg l^{-1}		µg l^{-1}		µg l^{-1}	
Fe	82	<72	1047	398 ± 80	922	353 ± 117
Mn	<3	<161	26	<176	6	<260
Ti	n.d	<311	n.d	<341	n.d	<503
Al	<100	<55	<100	<60	<100	<89
Rb	n.d	<4.2	n.d	<5.6	n.d	<6.8
Cd	<25	<0.4	<25	<0.4	<25	<0.4
Pb	<200	<10	<200	<11	<200	<17
		±2.1		±2.3		±3.4
Ba	3	5.2	8	8	8	8.4
Co	<20	<2.1	<20	2.3	<20	<3.4
La	<20	<2.1	<20	<2.3	<20	<3.4
Li	18	21.8	19	20.5	29	30.2
Nb	n.d	<2.1	n.d	<2.3	n.d	<3.4
Ni	<100	2.1	<100	<2.3	<100	<3.4
Sc	<2	<2.1	<2	<2.3	<2	<3.4
V	<20	<2.1	<20	<2.3	<20	<3.4
Y	<2	<2.3	<2	<2.3	<2	<3.4
Zr	<15	<2.3	<15	<2.3	<15	<3.4
		±5.2		±5.7		±8.4
Cr	<30	15.6	<30	14.8	<30	11.7
Cu	<10	<5.2	<10	<5.7	<10	<8.4
Zn	<20	<5.2	<20	<5.7	<20	<8.4
		±9.4		±10.2		±15.1
Ce	n.d	<9.4	n.d	<10.2	n.d	<15.1
Mo	<100	<9.4	<100	<10.2	<3	<15.1
I.B	1.5%	8.4%	2.5%	15%	0.7%	-
T_{min}	975		1402		2108	
C.F	0	96	0	87	0	59

Table 2.1A

Sample Set A continued

	SPALDING BULB		DEEP. ST. NICK		MOULTON W FEN	
	ARL	P	ARL	P	ARL	P
	mg l^{-1}		mg l^{-1}		mg l^{-1}	
Na	740	617	919	860	2060	2451
K	4.5	2.6	5.6	3.7	12	10
Ca	8	7	6	5	43	48
Mg	6.9	6.6	5.7	5.5	34.6	37.6
Si	2.8	<8	3.1	<10	2.9	<32
Sr	0.86	0.49	0.76	0.66	4.7	5.3
SO_4	26	23	18	18	117	137
	µg l^{-1}		µg l^{-1}		µg l^{-1}	
Fe	424	<128	222	<166	355	<479
Mn	14	<285	4	<368	13	<1061
Ti	n.d	<578	n.d	<710	n.d	<2053
Al	<100	<97	457	<126	21	<363
Rb	n.d	<3.7	n.d	<4.8	n.d	<13.7
Cd	<25	<0.7	<25	<1	<25	<3
Pb	<200	<18	<200	<24	<200	<76
		±3.7		±4.8		±13.7
Ba	9	9.2	7	9.5	45	61.7
Co	<20	<3.7	<20	<4.3	<20	<13.8
La	<20	<3.7	<20	<4.3	<20	<13.8
Li	37	40.5	41	45	117	199
Nb	n.d	<3.7	n.d	<4.8	n.d	<13.7
Ni	<100	<3.7	<100	<4.8	<100	<13.7
Sc	<2	<3.7	<2	<4.8	<2	<13.7
V	<20	<3.7	<20	<4.8	<20	<13.7
Y	<2	<3.7	<2	<4.8	<2	<13.7
Zr	<15	<3.7	<15	<4.8	<15	<13.7
		±9.2		±11.9		±34.3
Cr	<30	11.0	<30	16.7	<30	144
Cu	<10	<9.2	<10	<11.9	<10	<34.3
Zn	<20	<9.2	<20	<11.9	<20	41
		±16.6		±21.4		±61.7
Ce	n.d	<16.6	n.d	<21.4	n.d	<61.7
Mo	<100	<16.6	<100	<21.4	100	<61.7
I.B.	0.9%	8.7%	-1.1%	-4.5%	<0.1%	8.4%
T_{min}	2179		2695		5792	
C.F	0	5·1	0	4·2	0	1·4

Table 2.1A

Sample Set B

	QUAD. HI. FEN		CHEAL BRIDGE		SURFLEET		PINCHBECK WEST	
	ARL	P	ARL	P	ARL	P	ARL	P
	mg l^{-1}		mg l^{-1}		mg l^{-1}		mg l^{-1}	
Na	79	n.d	173	147	334	261	435	517
K	1.8	1.1	2.4	1.4	2.6	1.6	3.2	2.6
Ca	50	49	20	14	4	4	15	17
Mg	16	15	14	17	3.5	3.0	10	11
Si	3.8	n.d	3.9	4.3	3.5	3.6	4.2	<7
Sr	1.76	1.71	1.58	0.98	0.45	0.38	1.3	1.3
SO_4	37	41	28	24	20	19	35	30
	µg l^{-1}		µg l^{-1}		µg l^{-1}		µg l^{-1}	
Fe	120	70 ± 33	150	61 ± 41	18.9	<56	99	<86
Mn	2	<80	2.2	<91	0.4	<125	1.2	<190
Ti	n.d	<149	n.d	<176	n.d	<242	n.d	<369
Al	<3	88 ± 25	<3	46 ± 31	3	<43	<3	<65
Rb	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Cd	<1	n.d	<1	n.d	<1	n.d	<1	n.d
Pb	<10	n.d	<10	n.d	<10	n.d	<10	n.d
		±1		±1.2		±1.6		±2.5
Ba	18	23	11	12.9	2	5.6	9	14.7
Co	<0.8	<1	<0.8	2.3	<0.8	<1.6	<0.8	2.5
La	<1	6	<1	2.9	<1	<1.6	<1	2.5
Li	5.9	14	11.2	16.4	14.1	22.6	16.7	29.5
Nb	n.d	2	n.d	1.2	n.d	<1.6	n.d	<2.5
Ni	<1	<1	<1	1.8	<1	<1.6	<1	<2.5
Sc	<0.05	<1	<0.05	<1.2	<0.05	<1.6	<0.05	<2.5
V	<0.2	2	<0.2	1.2	<0.2	<1.6	<0.2	<2.5
Y	<0.05	1	<0.05	<1.2	<0.05	<1.6	<0.05	<2.5
Zr	<0.5	<1	<0.5	<1.2	<0.5	<1.6	<0.5	<2.5
		±2.4		±2.9		±4.0		±6.1
Cr	<1	15.2	<1	23.4	<1	11.3	<1	33.1
Cu	<0.3	2.4	<0.3	2.9	<0.3	<4.0	<0.3	6.1
Zn	19	31.8	<2	14.1	2	<50.8	<2	<6.1
		±4.3		±5.3		±7.2		±11.0
Ce	n.d	9.5	n.d	5.8	n.d	<7.2	n.d	<11.0
Mo	<3	<4.3	<3	<5.3	<3	<7.2	<3	<11.0
I.B	1.1%	-	1.7%	-4.8%	<0.1%	12%	0.5%	8.8%
T_{min}	551		713		1087		1384	
C.F	20	20	20	17	20	12	20	8·1

Table 2.1A

Sample Set B continued

	DONINGTON		GOSBERTON		SPALDING BULB	
	ARL	P	ARL	P	ARL	P
	mg l^{-1}		mg l^{-1}		mg l^{-1}	
Na	492	571	710	642	695	542
K	3.0	2.4	4.2	3.3	3.9	3.3
Ca	6	7	8	7	6	6
Mg	5.9	6.9	6.9	7.4	5.1	6.0
Si	1.6	<7	3.5	<9	1.4	<7
Sr	0.72	0.85	0.90	0.93	0.67	0.77
SO_4	0.3	1.2	4.9	1.7	26	13
	µg l^{-1}		µg l^{-1}		µg l^{-1}	
Fe	369	267 ± 107	1070	637 ± 141	133	<117
Mn	14.1	<236	6.8	<313	14.1	<260
Ti	n.d	<458	n.d	<616	n.d	<503
Al	<3	<18	4	<107	<3	<90
Rb	n.d	n.d	n.d	n.d	n.d	n.d
Cd	<1	n.d	<1	n.d	<1	n.d
Pb	<10	n.d	<10	n.d	<10	n.d
		±3.1		±4.0		±3.4
Ba	7	9.2	6	14.2	7	8.4
Co	<0.8	<3.1	<0.8	4.0	<0.8	<3.4
La	<1	<3.1	<1	4.0	<1	3.4
Li	15.9	29.0	25.6	40	29.2	33.5
Nb	n.d	<3.1	n.d	4.0	n.d	3.4
Ni	<1	<3.1	<1	<4.0	<1	<3.4
Sc	<0.05	<3.1	<0.05	<4.0	<0.05	<3.4
V	<0.2	<3.1	<0.2	<4.0	<0.2	<3.4
Y	<0.05	<3.1	<0.05	<4.0	<0.05	<3.4
Zr	<0.5	<3.1	<0.5	<4.0	<0.5	<3.4
		±7.6		±10.1		±8.4
Cr	<1	19.8	<1	20.2	<1	21.8
Cu	<0.3	<7.6	0.7	<10.1	<0.3	<8.4
Zn	2	<7.6	2	<10.1	<2	<8.4
		±13.7		±18.2		±15.1
Ce	n.d	<13.7	n.d	<18.2	n.d	<15.1
Mo	<3	<13.7	<3	<18.2	<3	<15.1
I.B	1.9%	9.3%	1.3%	-3.5%	1%	-10%
T_{min}	1461		2048		2019	
C.F	20	65	20	48	20	59

Table 2.1A

Sample Set B continued

	DEEP. ST. NICK		BICKER		MOULTON W FEN		CROWLAND BR	
	ARL	P	ARL	P	ARL	P	ARL	P
	mg l^{-1}		mg l^{-1}		mg l^{-1}		mg l^{-1}	
Na	926	918	1438	1279	1949	1946	1202	1107
K	5.4	4.7	7.5	5.3	12	9	7	4.7
Ca	5	5	17	19	47	42	9	9.4
Mg	5.3	5.4	12.4	13.2	35	33	14.4	14.9
Si	2.0	<11	3.7	<17	3.2	<23	2.2	<3.1
Sr	0.74	0.71	1.8	1.9	5.0	4.6	1.6	1.5
SO_4	40	13	0.7	1.4	132	170	106	96
	µg l^{-1}		µg l^{-1}		µg l^{-1}		µg l^{-1}	
Fe	28.5	<185	936	555 ± 277	120	<378	152	209
Mn	2.7	<410	3.1	<614	3.3	<837	4.2	<462
Ti	n.d	<1271	n.d	<1181	n.d	<1617	n.d	<358
Al	<5	<140	<3	<210	21	<143	111	237 ±158
Rb	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Cd	<1	n.d	<1	n.d	<1	n.d	<1	n.d
Pb	<10	n.d	<10	n.d	<10	n.d	<10	n.d
		±5.3		±7.9		±10.8		±6
Ba	5	44.9	24	35.7	30	54.0	13	18
Co	<0.8	<5.3	<0.8	<7.9	<0.8	<10.8	<0.8	6
La	<1	<5.3	<1	<7.9	<1	<10.8	<1	6
Li	35.1	58.2	56.0	83.3	116	152	58.5	72
Nb	n.d	<5.3	n.d	<7.9	n.d	<10.8	n.d	<6
Ni	<1	<5.3	<1	<7.9	<1	<10.8	<1	<6
Sc	<0.05	<5.3	<0.05	<7.9	<0.05	<10.8	<0.05	<0.6
V	<0.2	<5.3	<0.2	<7.9	<0.2	<10.8	<0.2	<6
Y	<0.05	<5.3	<0.05	<7.9	<0.05	<10.8	<0.05	<6
Zr	<0.5	<5.3	<0.5	<7.9	<0.5	<10.8	<0.5	<6
		±13.2		±19.8		±27.0		±14.9
Cr	<1	15.9	<1	59.5	<1	108	<1	14.9
Cu	<0.3	<13.2	0.9	<19.8	6.3	<27.0	0.8	<14.9
Zn	<2	15.9	50	55.5	140	119	629	1906
		±23.8		±35.7		±48.6		±26.9
Ce	n.d	<23.8	n.d	<35.7	n.d	<48.6	n.d	<26.9
Mo	<3	<23.8	<3	<35.7	<3	<48.6	<3	<26.9
I.B.	-0.3%	0.5%	0.2%	-5%	-1.5%	2.1%	0.5%	3.3%
T_{min}		2679		4039		5570		3487
C.F	20	37	20	25	20	18	20	29

Table 2.2A

RARE EARTH ELEMENTS AND YTTRIUM ($\mu g\ l^{-1}$) IN GROUNDWATERS FROM THE LINCOLNSHIRE LIMESTONE

	DEEP ST NICK	MOULTON W FEN	CROWLAND BR	SPALDING B CO
La	<0.176	1.10 ± 0.02	0.63 ± 0.01	0.414 ± 0.007
Ce	1.97 ± 0.05	4.0 ± 0.1	0.92 ± 0.02	0.40 ± 0.01
Pr	<0.98	<2	<1.23	<0.66
Nd	0.495 ± 0.004	0.536 ± 0.004	0.303 ± 0.002	0.148 ± 0.001
Sm	0.260 ± 0.002	<0.221	<0.136	<0.074
Eu	<0.041	<0.084	<0.056	<0.028
Gd	<0.735	<1.505	<0.928	<0.050
Dy	<0.182	<0.373	<0.230	0.242 ± 0.003
Ho	<0.081	<0.166	0.094 ± 0.004	<0.124
Er	<0.240	<0.491	<0.302	0.195 ± 0.003
Yb	<0.117	<0.240	0.154 ± 0.001	0.185 ± 0.003
Lu	<0.036	<0.074	<0.046	0.028 ± 0.001
Y	<0.089	0.375 ± 0.006	1.32 ± 0.02	2.62 ± 0.04
C.F	187	91	148	274

Notes

The analyses of the groundwater residue solutions (see 4.3) were carried out on the Philips ICP system.

C.F. refers to the concentration factors achieved

Table 2.2A

	CHEAL BRIDGE	PINCHBECK WEST	GOSBERTON	BICKER
La	0.046 ± 0.001	0.124 ± 0.002	<0.150	<0.270
Ce	0.163 ± 0.004	<0.213	<0.393	<0.533
Pr	<0.219	<0.450	<0.831	<1.50
Nd	0.026 ± 0.001	<0.016	<0.029	<0.052
Sm	0.024 ± 0.001	<0.050	<0.092	<0.166
Eu	<0.024	<0.019	<0.035	<0.063
Gd	<0.165	<0.339	<0.626	<1.13
Dy	0.096 ± 0.001	<0.084	<0.155	<0.280
Ho	<0.018	<0.037	<0.069	<0.125
Er	<0.054	<0.111	<0.204	<0.369
Yb	<0.026	<0.054	<0.100	<0.180
Lu	<0.008	<0.167	<0.031	<0.056
Y	0.62 ± 0.01	0.084 ± 0.002	<0.076	2.39 ± 0.04
C.F	837	407	220	122

Notes contd.

"Less than" values are equivalent to the LQDCs presented in table 3.5A, ± values are equivalent to the RSDs presented in table 3.1A.

Table 2.3A

COMPARISON OF GROUNDWATER ANALYSES (DIRECT DETERMINATIONS) CARRIED OUT BY THE ARL AND PHILIPS ICP-OES INSTRUMENTS

	SIXSCORE FM.		GIBBS FM.		ORCH. VILLA		BERTIE FEN	
	ARL	P	ARL	P	ARL	P	ARL	P
Na	275	281	98	108	741	706	152	148
Ca	8.6	7.0	74	64	8.0	6.8	29	24
Mg	6.3	5.5	15	14	5.5	4.9	16	14
K	1.8	2.4	2.2	2.9	2.8	3.5	1.6	2.2
Sr	0.8	0.7	1.5	1.3	0.8	0.7	1.8	1.5
Li	0.02	0.01	0.04	0.03	0.03	0.03	0.02	0.01
B	1.3	1.3	0.60	0.57	2.4	2.3	0.68	0.61

	RISEGATE		BLACK HOLE DR.		NEWLANDS FM.		CUCKOO BR.	
	ARL	P	ARL	P	ARL	P	ARL	P
Na	114	107	220	208	400	378	303	289
Ca	42	35	29	24	4.8	4.0	7.7	6.3
Mg	17	15	7.9	6.6	3.7	3.2	3.7	3.1
K	1.3	2.0	1.8	2.4	1.9	2.5	1.8	2.4
Sr	1.9	1.6	0.84	0.71	0.48	0.41	0.45	0.38
Li	0.02	<0.01	0.02	0.02	0.03	0.02	0.02	0.01
B	0.50	0.45	1.3	1.1	1.9	1.8	1.5	1.4

	CHEAL BR.		DEEP. ST. NICK		QUAD. HI. FEN		GOSBERTON	
	ARL	P	ARL	P	ARL	P	ARL	P
Na	166	168	2093	1979	77	84	671	762
Ca	23	18	13	11	57	48	9.4	7.7
Mg	15	13	7.0	6.1	18	15	7.6	6.4
K	1.8	2.3	3.9	4.8	1.8	1.8	2.0	4.0
Sr	1.6	1.4	1.1	0.93	2.0	1.7	0.99	0.84
Li	0.02	0.01	0.04	0.03	<0.01	<0.01	0.03	0.02
B	0.76	0.71	3.0	2.9	0.33	0.30	2.3	2.2

	SURFLEET		SPALDING BULB		MOULTON W. FEN		
	ARL	P	ARL	P	ARL	P	Corr. Coeff.
Na	322	330	650	632	1958	2094	0.996
Ca	5.0	4.2	7.7	6.4	56	50	0.999
Mg	3.9	3.4	5.3	4.6	36	35	0.997
K	2.1	2.5	2.6	3.6	9.3	11	0.993
Sr	0.46	0.42	0.71	0.64	5.4	5.3	0.998
Li	0.02	0.01	0.03	0.03	0.12	0.11	0.987
B	1.6	1.5	2.6	2.5	3.3	3.4	0.998

APPENDIX 3

PRECISION, BACKGROUND EQUIVALENT CONENTRATIONS AND DETECTION LIMITS FOR THE ANALYSIS OF LINCOLNSHIRE LIMESTONE ROCK CORE AND GROUNDWATERS BY ICP-OES

Table 3.1A Relative standard deviations (RSDS)

Table 3.2A Background equivalent concentrations (BECs)

Table 3.3A Aqueous three sigma detection limits

Table 3.4A Three sigma detection limits in the sample

Table 3.5A Lowest quantitatively determinable concentration in the sample (LQDCs)

Summary of sample preparation procedures and analytical programs used for the analysis of rock and groundwater residue samples on the Philips PV8490 ICP system

Analysis program	Dilution factor	Sample preparation	Samples
Major elements	500	$LiBO_2$ fusion	rocks
	2000	$LiBO_2$ fusion	residues
Trace elements	100	$HF/HClO_4$ digestion	rocks and residues
Rare earth elements	10	$HF/HClO_4$ digestion and REE separation from matrix on cation-exchange column	rocks and residues

Table 3.1A

PRECISION MEASUREMENTS (RSDs) FOR ANALYSIS BY ICP-OES

ICP system	Philips PV4890					ARL34000C	
Analysis Program	Major Elements		Trace Elements	Rare Earth Elements		Water Analysis	
Dil. F.+	500	2000	100	10		0	
Element	RSD%*	RSD%	RSD%	Element	RSD%	Element	RSD%
SiO2	**3.8**	**3.6**	-	La	3.4	Na	0.79
Al2O3	4.3	4.1	2.2	Ce	5.0	K	1.75
Fe2O3	3.6	7.8	1.5	Pr	1.5	Ca	1.00
MgO	4.6	7.3	2.1	Nd	1.5	Mg	0.91
CaO	**4.7**	2.7	1.9	Sm	1.8	B	1.14
Na2O	7.0	**5.3**	2.3	Eu	1.8	Li	1.18
K2O	6.6	2.3	3.0	Gd	0.5	SO4	0.69
TiO2	4.0	3.0	1.6	Dy	1.9	Si	1.03
P2O5	6.8	4.4	4.1	Ho	0.8	P	3.30
MnO	4.0	2.6	4.6	Er	2.9	Sc	0.94
NiO2	9.0	4.9	-	Yb	3.2	Sr	0.72
Cr2O3	9.2	7.8	-	Lu	2.4	Y	0.73
Ba	5.3	3.7	1.7	Y	3.1	Ba	0.98
Ce	-	-	3.0			Mn	0.68
Co	-	-	5.4			Co	0.80
Cr	-	-	3.9			Fe	0.57
Cu	-	-	3.5			V	1.23
La	-	-	1.5			Cd	0.58
Li	-	-	4.3			Zr	0.70
Mo	-	-	0.9			Cu	0.96
Nb	-	-	2.1			Zn	0.84
Ni	-	-	3.0			La	0.88
Sc	-	-	1.7			Cr	0.99
Sr	-	-	1.61			Ni	1.68
V	-	-	1.40			Mo	1.18
Y	-	-	1.50			Al	1.77
Zn	-	-	7.00			Pb	2.15
Zr	-	-	1.63				
Mean RSD	5.4%	4.5%	2.17%		2.3%		1.2%

Dil. F.+ = Dilution Factor

RSD* Relative Standard Deviation = 100 s / X

The majority of elements in the residues and rocks were determined in the "trace element solutions" (100-times dilution), the exceptions are in bold type: Si and Ca in the rock samples (major element solutions, 500 dilution factor) and Si and Na in the residue solutions (2000 times dilution factor)

Table 3.2A

BACKGROUND EQUIVALENT CONCENTRATIONS FOR ANALYSIS BY ICP-OES

ICP system	Philips PV4890			ARL34000C	
Analysis	Traces	REEs		Waters	
	mg kg^{-1}		mg kg^{-1}		mg l^{-1}
Si	*8400	La	0.43	Na	0.93
Al	*662	Ce	0.18	K	4.99
Ca	*573	Pr	0.57	Ca	0.97
Fe	*210	Nd	2.63	Mg	1.61
Mg	*843	Sm	0.45	B	0.29
Na	*37	Eu	0.04	Li	0.10
K	*456	Gd	1.09	SO4	5.01
Ti	*181	Dy	0.12	P	1.81
P	*22	Ho	0.09	Si	1.03
Mn	*55	Er	0.22	Sr	0.009
Ba	4.2	Yb	0.22	Be	0.03
Ce	77	Lu	0.06	Ba	0.03
Co	9	Y	0.10	Sc	0.03
Cr	26			Sr	0.03
Cu	65			Mn	0.05
La	17			Co	0.19
Li	27			Fe	0.13
Ni	16			Zn	0.16
Nb	14			V	0.16
Sc	2			Cd	0.24
Sr	2			La	0.16
V	21			Cu	0.11
Y	8			Zr	0.17
Zn	11			Ni	0.65
Zr	174			Mo	0.68
				Al	1.52
				Pb	2.54

* The values for Si to Mn in rock samples are converted from weight percent oxide data.

Table 3.3A

AQUEOUS THREE SIGMA DETECTION LIMITS FOR ICP-OES

ICP system	Philips PV4890	ARL34000C
Analysis	Rocks	Waters
Element	mg kg^{-1}	mg l^{-1}
Si	*2.24	0.013
Al	*0.37	0.022
Ca	*1.30	0.013
Fe	*0.38	0.003
Mg	*0.25	0.029
Na	*0.014	0.009
K	*0.2	0.086
P	*0.011	0.076
Mn	*0.035	0.0008
Ni	0.0072	0.019
Cr	0.022	-
Ba	0.0002	0.0005
Co	0.0028	0.005
Cu	0.037	0.003
Li	0.006	0.0013
Nb	0.004	-
Sc	0.0019	0.0005
Sr	0.0007	0.0004
V	0.0039	0.002
Zn	0.0153	0.007
Zr	0.087	0.003
B	-	0.0003
SO4	-	0.076
Cd	-	0.006
La	0.004	0.003
Ce	0.0013	-
Pr	0.007	-
Nd	0.006	-
Sm	0.0034	-
Eu	0.005	-
Gd	0.0051	-
Dy	0.0011	-
Ho	0.0008	-
Er	0.0018	-
Yb	0.001	-
Lu	0.0002	-
Y	0.0012	-

* Detection limits for Si to Mn in rock solutions are converted from weight percent oxide data

Table 3.4A

THREE SIGMA DETECTION LIMITS FOR ICP-OES IN THE SAMPLE

ICP system	Philips PV4890			ARL34000C	
Analysis program	Traces		REEs		Waters
	mg kg^{-1}		mg kg^{-1}		mg l^{-1}
Si	*4487	La	0.04	Na	0.009
Al	*37	Ce	0.013	K	0.086
Ca	*130	Pr	0.07	Ca	0.013
Fe	*38	Nd	0.06	Mg	0.029
Mg	*25	Sm	0.034	B	0.0003
Na	*1.4	Eu	0.05	Li	0.0013
K	*20	Gd	0.051	SO4	0.076
Ti	*4.1	Dy	0.011	P	0.076
P	*1.1	Ho	0.008	Si	0.013
Mn	*3.5	Er	0.018	Sr	0.0001
		Yb	0.01	Be	0.0002
Ba	0.02	Lu	0.002	Ba	0.0005
Ce	2.2	Y	0.012	Sc	0.0005
Co	0.28			Sr	0.0004
Cr	2.2			Mn	0.0008
Cu	3.70			Co	0.005
La	0.70			Fe	0.003
Li	0.72			Zn	0.007
Ni	0.60			V	0.002
Nb	0.40			Cd	0.006
Sc	0.19			La	0.003
Sr	0.07			Cu	0.003
V	0.39			Zr	0.003
Y	0.86			Ni	0.019
Zn	1.53			Mo	0.025
Zr	174			Al	0.022

$D.L^{+}$: three sigma detection limit in the sample, allowing for appropriate dilution factors.

* The values for Si to Mn in rock samples are converted from weight percent oxide data.

Table 3.5A

LOWEST QUANTITATIVELY DETERMINABLE CONCENTRATIONS (LQDCs) FOR ICP-OES USED FOR THE ANALYSIS OF ROCK AND WATER SAMPLES FROM THE LINCOLNSHIRE LIMESTONE AQUIFER

ICP system	Philips PV4890		ARL34000C		
Analysis program	Traces		REEs		Waters
Element	mg kg^{-1}	element	mg kg^{-1}	element	mg l^{-1}
Si	*468	La	0.33	Na	0.05
Al	*53	Ce	0.865	K	0.43
Ca	*143	Pr	1.83	Ca	0.06
Fe	*70	Nd	0.063	Mg	0.02
Mg	*121	Sm	0.203	B	0.001
Na	*74	Eu	0.077	Li	0.007
K	*83	Gd	1.38	SO4	0.380
Ti	*300	Dy	0.342	P	0.038
P	*109	Ho	0.152	Si	0.065
Mn	*155	Er	0.45	Sr	0.001
Ni	2	Yb	0.22	Be	0.001
Cr	5	Lu	0.068	Ba	0.003
		Y	0.12	Sc	0.003
Ba	2			Sr	0.003
Ce	9			Mn	0.004
Co	2			Co	0.026
Cu	5			Fe	0.013
La	2			Zn	0.033
Li	2			V	0.012
Mo	9			Cd	0.028
Nb	2			La	0.014
Sc	2			Cu	0.016
Sr	2			Zr	0.017
V	2			Ni	0.097
Y	2			Mo	0.125
Zn	5			Al	0.111
Zr	2				

* The values for Si to Mn in rock samples are converted from weight percent oxide data, in most cases the LQDCs are equivalent to 0.02% oxide with the exceptions of SiO_2 (0.1%) and Ti_02 and P_2O_5 (0.05%)

LQDCs for the REEs are chondritic abundances with the exceptions of Ho, Er, Lu (2 times), Gd (5 times) and Pr (15 times)

The LQDCs for the ARL system are five times the three sigma detection limit

APPENDIX 4

ANALYSES OF ROCK CORE FROM THE LINCOLNSHIRE LIMESTONE AND ASSOCIATED STRATA FROM SOUTHERN LINCOLNSHIRE

Table 4.1A Analyses of rock core from Bicker borehole

Table 4.2A Analyses of rock core from Donington borehole

Table 4.3A Analyses of rock core from Moulton West Fen borehole

Table 4.4A Anayses of rock core from Billingborough borehole

Notes

Core from Bicker and Donington borehole was provided by D. Emery, core from Moulton West Fen and Billingborough boreholes was provided by BGS

The detection limits and precision appropriate to the determinations are presented in tables 3.5A and 3.1A respectively.

Depths below ground level are indicated where known; ground level is at approximately 3 m above Ordnance Datum at Bicker, Donington and Moulton West Fen boreholes

Stratigraphic details are also presented: Blis. Lst = Blisworth Limestone, U.E.S. = Upper Estuarine Series, G.F. = Grantham Formation

Table 4.1A

ANALYSES FOR ROCK SAMPLES FROM BICKER BOREHOLE

Element	Sample							
	B1	B2	B3	B4	B5	B6	B7	B8
weight percent								
Ca	33	27	0.8	30	29	36	37	37
Si	1.7	9	40	2	7	0.74	0.11	0.38
Al	0.40	1.24	2.43	0.45	0.53	0.12	0.06	0.09
$\mu g\ kg^{-1}$								
Ba	32	76	28	30	66	15	8	13
Co	18	19	11	25	14	15	15	15
Cr	<5	35	63	22	8	<5	<5	<5
Cu	20	18	9	13	15	13	12	13
Fe	11190	11331	5805	15737	4616	2728	1784	2868
K	1079	3985	415	996	1411	291	125	249
Li	7	17	71	7	6	3	3	3
Mg	4584	6152	905	9529	3136	4222	4342	3920
Mn	465	620	<155	465	155	155	<155	232
Mo	<9	<9	<9	<9	<9	<9	<9	<9
Na	445	796	414	605	159	127	127	96
Nb	16	19	20	18	16	17	17	17
Ni	60	50	50	70	40	40	40	40
P	175	437	109	109	<44	<44	<44	<44
Rb	8	37	4	7	7	<2	<2	<2
Sc	4	7	17	17	3	3	3	3
Sr	553	504	79	799	413	450	495	370
Ti	360	480	4796	360	900	120	<120	240
V	22	67	124	51	22	21	17	17
Zn	<5	4	38	<5	<5	<5	<5	<5
Zr	14	83	683	45	106	8	<2	<2
La	14	36	210	168	5.8	3.0	3.1	2.6
Ce	25	69	574	382	11	5.9	5.0	4.5
Pr	3.7	7.9	45	33	<1.8	<1.8	<1.8	<1.8
Nd	13	34	250	184	5.5	3.1	2.9	2.5
Sm	2.4	6.6	45	32	1.1	0.66	0.64	0.51
Eu	0.51	1.5	8.7	6.3	0.15	0.14	0.15	0.11
Gd	<1.4	5.5	35	25	<1.4	<1.4	<1.4	<1.4
Dy	1.4	4.8	22	15	0.78	0.42	0.38	<0.34
Ho	0.41	1.1	3.9	2.9	0.26	<0.15	0.20	0.16
Er	1.4	3.1	10	7.4	0.85	0.52	0.97	0.51
Yb	0.70	1.9	6.3	4.2	0.55	0.24	0.29	0.27
Lu	0.10	0.27	0.85	0.57	0.09	<0.07	<0.07	<0.07
Y	7.8	27	84	68	4.7	7.0	0.3	1.7
(m)	97	99.3	106.6	107.3	111.0	112.3	113.1	114.3
Strat.	Blis. Lst.	U.E.S.		Lincolnshire Limestone Formation (UPPER)				

Table 4.1A

Element	Sample						
	B9	B10	B11	B12	B13	B14	B15
weight percent							
Ca	26	37	36	31	31	35	14
Si	7	0.20	0.24	5.6	4.7	0.98	23.4
Al	1.3	0.13	0.087	0.26	0.26	0.19	1.09
mg kg^{-1}							
Ba	77	8	8	41	29	15	262
Co	15	15	14	16	16	16	13
Cr	36	9	<5	14	8	<5	45
Cu	17	13	13	15	15	15	15
Fe	9617	2483	2168	7624	5526	6505	8288
K	3155	166	208	872	664	415	4690
Li	16	3	3	4	4	4	8
Mg	5126	3980	4222	3317	3317	3800	2111
Mo	<9	<9	<9	<9	<9	<9	15
Mn	155	155	155	232	232	310	310
Na	668	127	191	350	350	191	2164
Nb	19	15	15	14	14	15	15
Ni	50	40	40	45	45	40	36
P	<44	<44	<44	<44	<44	<44	44
Rb	25	<2	<2	4	3	2	24
Sc	6	3	2	4	5	3	5
Sr	413	368	345	347	394	474	353
Ti	1739	180	180	540	480	779	2640
V	56	19	14	44	40	36	45
Zn	7	<5	<5	<5	<5	<5	11
Zr	78	<3	<3	76	45	84	464
La	9.0	3.5	1.8	5.9	7.3	5.4	18
Ce	16	5.4	3.0	13	19	11	40
Pr	3	<1.8	<1.8	<1.8	2	<1.8	5
Nd	7.4	3.0	1.7	7.1	10	6.0	22
Sm	1.4	0.64	0.36	1.4	2.2	1.3	4.1
Eu	0.29	0.15	<0.08	0.32	0.46	0.28	0.80
Gd	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4	4
Dy	0.90	0.37	<0.23	1.1	1.5	1.0	3.1
Ho	0.39	0.21	<0.15	0.31	0.35	0.24	0.74
Er	1.3	0.80	<0.45	0.85	1.0	0.83	2.1
Yb	0.74	0.29	0.27	0.55	0.69	0.51	1.7
Lu	0.11	<0.07	<0.07	0.08	0.55	0.07	0.26
Y	4.9	2.2	1.4	5.5	7.0	5.6	18
(m)	118.1	119.6	125.4	129	130.5	131.8	133.3
Strat.	Lincolnshire Limestone Formation (MIDDLE) | (LOWER)						| G.F.

Table 4.2A

ANALYSES OF ROCK SAMPLES FROM DONINGTON BOREHOLE

Element	Sample				
	D1	D2	D3	D4	D5
weight percent					
Ca	23	21	23	8.9	19
Si	2.2	0.44	2.5	8.9	1.7
Al	0.18	0.058	0.23	0.77	0.16
mg kg^{-1}					
Ba	24	8	26	71	21
Co	15	15	15	15	15
Cr	6	<5	<5	16	<5
Cu	14	13	14	14	13
Fe	8498	3148	3112	4756	3078
K	374	125	623	1951	415
Li	4	2	4	9	4
Mg	5488	3800	4583	4101	3860
Mn	155	155	<155	155	155
Mo	<9	<9	<9	<9	<9
Na	255	96	159	222	159
Nb	15	17	18	18	17
Ni	38	38	40	40	40
P	<44	<44	<44	<44	<44
Rb	<2	<2	3	13	<2
Sc	26	2	3	4	2
Sr	539	489	471	376	445
Ti	300	180	480	1320	300
V	20	13	18	29	14
Zn	<5	<5	<5	<5	<5
Zr	24	8	38	145	19
La	93	4.7	5.6	7.9	2.4
Ce	191	5.6	7.3	15	3.8
Pr	18	<1.8	<1.8	<1.8	<1.8
Nd	90	3.0	3.6	7.1	2.0
Sm	17	0.59	0.75	1.3	0.37
Eu	3.7	0.16	0.16	0.25	0.09
Gd	16	<1.4	<1.4	<1.4	<1.4
Dy	14	0.90	0.58	1.1	<0.34
Ho	2.6	0.34	0.26	0.28	0.18
Er	6.9	0.82	1.1	0.91	<0.45
Yb	4.9	0.48	0.41	0.74	<0.22
Lu	0.64	0.08	<0.07	0.11	<0.07
Y	59	11	6.8	7.6	1.6
(m)	87	88.2	89	90	91
Strat.	Lincolnshire Limestone Formation (UPPER)				

Table 4.3A

ANALYSES OF ROCK SAMPLES FROM MOULTON WEST FEN BOREHOLE

Element	Sample			
	M1	M2	M3	M4
weight percent				
Ca	0.34	38	39	36
Si	40	0.33	0.38	1.0
Al	2.01	0.13	0.65	0.18
mg kg^{-1}				
Ba	128	11	5	11
Co	8	9	8	9
Cr	100	<3	<3	<3
Cu	16	13	16	17
Fe	3882	4372	1854	4546
K	4150	83	83	332
Li	88	8	4	8
Mg	2894	3800	2955	3619
Mn	155	<155	155	<155
Mo	11	<9	<9	<9
Na	764	159	127	159
Nb	31	9	7	9
Ni	23	20	13	25
P	<44	<44	<44	<44
Sc	13	<2	<2	<2
Sr	74	459	248	367
Ti	11990	600	180	300
V	81	10	7	26
Zn	10	<5	<5	<5
Zr	846	4	3	11
La	49	8.4	2.7	4.5
Ce	101	14	2.6	11
Pr	12	2.1	<1.8	<1.8
Nd	46	8.1	1.5	5.9
Sm	8.7	1.8	0.41	1.3
Eu	1.8	0.46	0.09	0.31
Gd	8.2	2.4	<1.4	<1.4
Dy	9.8	2.5	<0.45	1.3
Ho	2.1	0.55	0.11	0.29
Er	6.5	1.5	0.90	0.87
Yb	6.3	1.2	0.24	0.76
Lu	0.96	0.19	0.09	0.14
Y	56	16	3.4	8.4
(m)	98.6	100.3	102.2	109.1
Strat.	U.E.S. | Lincolnshire Limestone (UPPER)		|(LOWER)	

Table 4.4A

ANALYSES OF ROCK SAMPLES FROM BILLINGBOROUGH BOREHOLE

Element	Sample				
	BL1	BL2	BL3	BL4	BL5
weight percent					
CaO	41	42	41	41	42
SiO2	0.55	0.33	0.88	0.36	0.34
Al2O3	0.18	0.11	0.11	0.12	0.11
mg kg^{-1}					
Ba	9	6	5	7	5
Co	12	12	11	12	11
Cr	<5	<5	<5	<5	<5
Cu	15	15	16	16	15
Fe	3147	1958	1853	1678	1364
K	83	<83	<83	<83	<83
Li	3	3	3	3	3
Mg	3377	3438	3136	3196	3136
Mn	155	155	155	<155	<155
Mo	<9	<9	<9	<9	<9
Na	96	64	64	64	64
Nb	16	16	15	17	16
Ni	35	38	35	39	35
P	<44	<44	<44	<44	<44
Sc	<2	<2	<2	<2	<2
Sr	412	418	438	468	446
Ti	240	180	180	180	180
V	15	13	12	12	12
Zn	<5	<5	<5	<5	<5
Zr	25	14	20	14	15
La	n.d	n.d	0.32	n.d	1.96
Ce	n.d	n.d	0.52	n.d	1.04
Pr	n.d	n.d	<1.8	n.d	<1.8
Nd	n.d	n.d	0.53	n.d	1.5
Sm	n.d	n.d	<0.20	n.d	<0.20
Eu	n.d	n.d	<0.08	n.d	<0.08
Gd	n.d	n.d	<1.4	n.d	<2
Dy	n.d	n.d	<0.34	n.d	0.37
Ho	n.d	n.d	0.15	n.d	<0.15
Er	n.d	n.d	<0.45	n.d	0.70
Yb	n.d	n.d	<0.22	n.d	<0.22
Lu	n.d	n.d	<0.07	n.d	<0.07
Y	n.d	n.d	0.45	n.d	0.50
colour	buff	grey	grey	grey	buff

The samples are from approximately 23.9 m B.O.D.

APPENDIX 5

ANALYSES OF LINCOLNSHIRE LIMESTONE GROUNDWATERS COLLECTED BETWEEN MAY 1984 AND DECEMBER 1986

Table 5.1A December 1985

Table 5.2A March 1985

Table 5.3A September 1984

Table 5.4A May 1984

Determinations by ICP-OES (section 3.4) except:

pH, Eh, temperature, SEC (specific electrical conductance), O_2 and HCO_3 on site (section 2.3)

Br, I, Cl, NO_3-N - Technicon autoanalyser II (section 3.5)

F - ISE (ion selective electrode) (section 3.5)

Dissolved sulphide - ISE and ICP-OES (section 4.2)

Table 5.1A GROUNDWATERS - DECEMBER 1985

Site No.	Location	Grid reference	Date of sampling	Usage
1	Billingbrough, New Inn Ho	5117733432	301185	P.S.
2	Sempringham House Fm	5122333282	301185	over-flowing
3	Car Dyke Fm	5125132794	101285	P.S.
4	Dyke Fm	5111032130	091285	(irreg.)
5	Warners Printers, Bourne	5093032000	091285	P.S.
6	Klondyke Stud Fm, Bourne	5088731923	091285	pumped P.S.
7	Springfields, Bourne	5102231882	301185	P.S.
8	Northorpe Fen	5109231795	081285	P.S.
9	Kate's Bridge Nursery	5107331521	071285	P.S.
10	Wilsthorpe	5095131361	081285	obs.
11	Langtoft, The Croft	5120231283	081285	(irreg.)
12	Swaton Fen, Smiths	5150933769	031286	P.S.
13	Glebe Fm, Smiths	5164333686	031285	P.S.
14	Donington Westdale	5175733569	011285	P.S.
15	Billingborough Fen Fm	5161133380	301185	P.S.
16	Mornington House Fm	5172933174	011285	P.S.
17	Aslackby Fen, Barker's	5157933037	301185	P.S.
18	New House Fm, Morton Fen	5137132455	101285	P.S.
19	Twenty, Stables	5144032039	091285	P.S.
20	Black Ho Fm, Bourne S Fen	5133431903	081285	P.S.
21	Proctor's, Quad Hi Fen	5204433134	031285	P.S.
22	Daniel's, Quad Hi Fen	5198833152	041285	P.S.
23	Vicarage Fm	5176132817	021285	P.S.
24	Rigbolt House	5194732826	021285	over-flowing
25	Black Hole Drove	5178232514	061285	P.S.
26	Forty Ft Fm, Morton Fen	5169032370	101285	P.S.
27	Pinchbeck South Fen	5183032211	091285	over-flowing
28	Chimney Fm, Tongue End	5171031767	091285	over-flowing
29	Deeping Fen Fm	5152731646	071285	P.S.
30	Twopenny Cuts	5153031510	071286	P.S.
31	Sixscore Fm, Langtoft Fen	5166331415	071285	P.S.
32	Elm Fm, Langtoft Fen	5152031291	071285	P.S.
33	Gibbs Fm, Langtoft Fen	5142631281	071285	P.S.
34	Bicker, Golden Drove	5247233850	021285	obs.
35	Donington, Caythorpe Fm	5221133623	011285	obs.
36	Gosberton	5244433148	021285	obs.
37	Cheal Bridge	5226032936	041285	obs.
38	Risegate, Gotobed's	5215632898	041285	P.S.
39	Surfleet	5247932798	041285	obs.
40	Pinchbeck West	5211132713	041285	obs.
41	Newlands, Tydd Lane	5221532425	051285	P.S.
42	Spalding Bulb Co	5233132192	051285	obs.
43	Horseshoe Bridge	5218432115	051285	obs.
44	Cuckoo Bridge	5201331969	051285	obs.
45	Deeping St Nicholas	5222931798	061285	obs.
46	Orchard Villa, Deep St Nick	5212531598	061285	P.S.
47	Barron's Fm, Deep St James	5182431125	061285	P.S.
48	Crowland Bridge	5229831067	111285	obs.
49	Moulton West Fen	5288631583	111285	obs.
50	Seawater, The Wash	5558035775	141285	
45	Deeping St Nicholas	5222931798	020286	obs.

Usage: P.S. = private supply (domestic and/or irrigation, watering livestock etc.), obs. = A.W. observation borehole only

Table 5.1A

distance from outcrop	temp. °C	pH	Eh mV	dissolved oxygen mg l^{-1}	SEC µS cm^{-1}	site no.
17.6	-	7.40	-	-	785	1
18.2	10.4	7.05	-	-	815	2
18.2	9.8	6.95	+136	0.7	835	3
18.5	-	7.05	-	-	590	4
16.9	-	6.95	+390	-	885	5
16.4	10.1	6.80	+301	1.0	850	6
17.8	8.5	7.80	-	-	185	7
18.8	-	7.35	-	-	835	8
19.0	10.2	7.10	+131	0.2	765	9
17.6	10.7	7.20	+151	0.5	825	10
20.3	8.1	7.00	+39	0.4	775	11
20.6	11.6	7.33	+121	0.4	605	12
22.0	9.3	7.75	-29	0.3	395	13
23.3	10.8	7.95	-14	0.4	495	14
22.0	10.0	7.35	-	-	720	15
23.4	7.2	7.45	+96	0.5	540	16
22.3	11.3	7.05	+56	0.6	710	17
20.2	-	7.05	-	-	635	18
21.9	8.3	6.95	-	-	830	19
21.7	11.3	7.10	+116	0.2	740	20
26.0	-	7.70	-	-	560	21
26.8	11.6	7.40	+91	0.2	670	22
24.2	11.1	7.10	+125	<0.2	610	23
26.0	12.2	7.60	+51	0.3	710	24
24.8	11.1	7.75	+16	0.2	1110	25
26.8	9.8	7.00	+81	0.3	673	26
24.9	10.1	7.05	-	-	730	27
25.0	12.5	7.55	-	-	995	28
23.3	11.1	7.30	-	-	850	29
23.9	9.5	7.95	-	-	1230	30
24.7	11.9	8.00	+36	0.4	1230	31
23.6	10.9	7.35	+36	0.4	805	32
22.7	11.2	7.25	+151	0.2	780	33
29.9	9.9	8.25	-	-	5900	34
27.7	10.0	9.00	-154	0.3	1970	35
30.6	12.5	8.85	-114	0.2	3150	36
29.0	12.2	7.75	+41	0.4	920	37
28.0	11.3	7.45	+16	0.2	730	38
31.3	12.4	8.60	+1	0.3	1495	39
27.9	11.4	7.95	-4	0.4	1995	40
29.1	9.7	8.30	-54	0.1	1470	41
30.4	11.9	8.95	-29	0.3	2995	42
29.3	12.8	8.15	+91	0.4	1345	43
27.8	12.6	8.25	+141	0.4	1295	44
30.1	11.1	8.80	-84	0.2	4000	45
29.3	8.3	8.55	-	-	3000	46
27.0	11.0	7.95	+50	0.3	1010	47
31.7	9.5	8.65	-4	<0.2	5400	48
36.8	10.9	7.75	+80	<0.2	9450	49
-	12.9	7.75	-	-	37500	50
30.1	12.5	8.90	-49	<0.2	4450	45

Distance from outcrop (km) is measured along a transect (fig 5.1)

Table 5.1A

units - mg l^{-1}

Site	Na	K	Ca	Mg	HCO_3	SO_4	Cl	NO_3-N	Si
1	14	2.4	127	10.1	252	133	31	0.2	2.0
2	16	2.5	135	7.3	300	131	29	0.1	3.5
3	18	2.7	136	8.8	279	139	28	<0.1	3.1
4	16	3.3	86	10.8	222	103	20	<0.1	1.0
5	13	3.0	150	9.4	315	143	31	5.3	2.9
6	14	2.8	157	9.4	281	153	38	5.0	2.9
7	14	2.7	70	6.6	153	77	3	<0.1	1.4
8	19	3.1	146	10.2	337	165	30	<0.1	2.9
9	16	2.7	139	9.1	332	143	29	<0.1	2.9
10	15	2.3	153	8.0	322	155	30	<0.1	2.8
11	15	2.9	148	9.4	300	135	31	4.0	3.0
12	34	1.8	95	8.9	326	68	22	<0.1	3.4
13	31	1.6	53	8.9	239	12	25	<0.1	1.8
14	42	2.0	68	12.8	311	39	21	<0.1	3.6
15	17	1.8	120	7.9	284	122	25	<0.1	3.0
16	22	1.7	90	8.2	285	83	21	<0.1	3.2
17	20	1.7	104	8.9	286	83	22	<0.1	3.1
18	28	2.6	109	10.1	320	97	26	0.9	3.1
19	33	2.1	91	9.3	315	68	18	<0.1	3.4
20	28	2.4	112	13.6	305	108	25	<0.1	3.9
21	60	1.8	52	15.9	328	30	28	0.2	3.6
22	79	1.8	50	16.2	333	37	34	<0.1	3.8
23	61	1.8	61	16.1	323	41	27	<0.1	3.7
24	109	2.2	35	17.5	353	36	50	0.4	3.9
25	229	2.0	22	6.3	440	43	119	<0.1	3.5
26	77	2.1	86	16.8	334	51	26	<0.1	3.8
27	93	2.3	48	14.8	342	42	48	0.3	3.9
28	178	3.0	22	11.0	310	40	100	0.8	4.0
29	152	2.6	22	9.4	395	40	68	0.5	3.8
30	267	2.8	11	8.2	432	42	178	0.6	3.8
31	287	2.5	7	5.8	445	39	184	0.6	3.6
32	80	3.0	75	16.1	376	96	53	<0.1	3.8
33	76	3.2	85	16.7	300	92	45	<0.1	3.8
34	1438	7.5	17	12.4	668	1	1895	<0.1	1.8
35	492	3.0	6	5.9	464	0	490	<0.1	1.6
36	710	4.2	8	6.9	511	5	803	<0.1	3.5
37	173	2.4	20	14.0	387	28	89	<0.1	3.0
38	110	2.1	37	15.5	358	39	50	<0.1	3.9
39	334	2.6	4	3.5	481	20	242	<0.1	3.5
40	435	3.2	15	10.1	450	35	436	0.8	4.2
41	387	2.6	4	3.3	483	29	288	<0.1	3.1
42	695	3.9	6	5.1	533	26	750	<0.1	1.4
43	287	8.2	17	7.2	421	33	206	0.5	3.6
44	283	2.4	6	3.1	448	34	188	0.8	3.6
45	1926	5.4	5	5.4	617	40	1080	<0.1	2.0
46	697	3.8	6	4.6	551	41	750	0.9	2.8
47	246	3.1	15	9.9	420	59	145	<0.1	3.8
48	1202	7.0	9	14.4	652	106	1480	1.3	2.2
49	1949	12.7	47	34.7	422	132	2960	<0.1	3.2
50	12060	430	466	1530	155	3002	18100	<0.1	2.2
45	-	-	-	-	643	-	1100	-	-

Table 5.1A

units - $\mu g\ l^{-1}$

Sr	Ba	F	Br	I	Li	B	P	S	Site
815	15	110	107	6	5.6	63	135	0.8	1
468	19	227	106	3	7.1	540	115	-	2
488	15	145	98	7	3.9	50	232	11	3
362	11	95	138	3	7.6	37	71	-	4
403	18	225	98	3	12	55	160	1	5
431	16	116	115	4	7.9	36	207	0.2	6
285	10	140	110	5	6.7	77	41	0	7
526	16	180	96	9	9.0	95	118	3	8
511	14	190	108	5	3.4	50	226	6	9
450	17	200	114	3	3.4	31	228	65	10
405	14	140	72	8	5.2	37	224	0.6	11
530	15	470	90	17	1.9	117	193	2	12
615	11	440	105	15	3.9	83	157	2	13
1050	20	600	94	25	3.9	124	192	41	14
466	21	245	115	8	1.9	42	159	32	15
562	19	600	81	9	4.9	115	157	0	16
615	17	500	85	14	1.8	63	185	6	17
673	15	130	89	5	8.9	98	114	23	18
630	13	330	85	4	6.4	90	166	4	19
1070	18	390	98	15	5.8	117	230	10	20
1370	34	1000	126	28	8.5	227	135	-	21
1760	18	1100	150	35	5.9	301	298	19	22
1650	21	970	131	28	5.4	230	255	2	23
2050	20	1370	223	45	9.4	516	245	18	24
696	11	2050	525	109	15.7	1160	333	4	25
1710	23	1130	122	13	14.7	376	282	80	26
1620	3	1370	208	45	15.0	396	77	4	27
1220	13	2050	670	116	19	874	238	5	28
970	25	1700	298	62	14	813	182	6	29
921	29	2050	750	157	14	1060	253	15	30
713	7	3900	900	152	13	1170	377	5	31
1750	22	950	218	32	9.4	411	230	21	32
1670	20	930	173	13	9.4	368	244	2	33
1830	24	2900	8900	958	56	3389	818	4	34
715	7	3300	2125	338	16	1820	414	1	35
903	6	3700	3300	460	26	2230	545	7	36
1580	11	2170	390	76	11	629	344	7	37
1770	17	1320	211	45	8.8	392	263	16	38
448	2	3450	1010	182	14	1370	376	8	39
1303	9	3000	1888	579	16.7	1850	424	26	40
440	3	4600	1250	18	15	1670	411	8	41
674	7	4500	3750	539	29	2650	544	47	42
855	7	3050	870	162	15	1180	328	3	43
385	1	3100	850	129	13	1240	329	4	44
744	5	3300	5150	700	35	2980	715	95	45
644	8	2600	3350	531	26	2370	516	1	46
1250	8	2300	690	122	15	1030	290	10	47
1600	12	2600	6825	991	59	2490	885	0	48
5010	30	1800	15000	1634	116	3329	1100	14	49
8240	84	1700	78000	-	226	5100	-	-	50
-	-	3600	5550	728	-	-	-	76	45

Table 5.1A

units - $\mu g\ l^{-1}$

Site	Fe	Mn	Cu	Zn	V	
1	332	6.9	3.2	51	<0.2	PF
2	104	2.7	<0.3	7	0.5	F
3	793	5.7	<0.3	<2	<0.2	P
4	-	-	-	-	-	F
5	-	-	-	-	-	F
6	28	1.9	2.3	38	0.6	
7	821	25.4	3.0	24	<0.2	F
8	250	5.7	1.3	8	<0.2	F
9	326	5.9	<0.3	3	<0.2	
10	394	3.8	<0.3	3	1.0	
11	5.8	2.2	3.4	10	0.5	
12	147	1.9	4.7	8	<0.2	
13	1690	28.5	17.4	6	<0.2	
14	545	7.8	<0.3	<2	<0.2	
15	-	-	-	-	-	F
16	2520	14.5	0.7	139	<0.2	P
17	283	2.4	<0.3	9	0.2	
18	533	4.6	5.8	<0.3	<0.2	F
19	272	4.0	<0.3	141	<0.2	F
20	138	3.3	<0.3	4	<0.2	
21	-	-	-	-	-	PF
22	120	1.6	<0.3	19	<0.2	
23	68	1.0	0.3	<2	<0.2	
24	129	1.5	<0.3	<2	<0.2	
25	863	3.0	<0.3	37	<0.2	
26	420	2.8	<0.3	24	<0.2	P
27	<0.5	<0.2	<0.3	37	<0.2	F
28	65	0.6	0.4	5	<0.2	F
29	8.0	2.4	<0.3	68	<0.2	F
30	67	0.4	0.7	153	<0.2	F
31	27	0.2	<0.3	13	<0.2	
32	3180	20.3	<0.3	<2	<0.2	
33	141	1.4	<0.3	3	<0.2	
34	936	3.1	0.9	50	<0.2	F
35	369	14.1	<0.3	<2	<0.2	
36	1070	6.8	0.7	2	<0.2	P
37	151	2.2	<0.3	<2	<0.2	
38	380	2.4	<0.3	<2	<0.2	
39	19	0.4	<0.3	2	<0.2	
40	99	1.2	<0.3	<2	<0.2	
41	173	1.4	<0.3	8	<0.2	
42	133	14.1	<0.3	<2	<0.2	
43	22	0.6	<0.3	3	<0.2	
44	66	1.9	<0.3	<2	<0.2	
45	392	3.7	0.7	12	<0.2	
46	29	2.7	<0.3	<2	<0.2	PF
47	42	0.6	<0.3	51	<0.2	
48	169	4.2	0.8	629	<0.2	
49	120	3.3	6.3	140	<0.2	
50	-	-	-	-	-	
45	-	-	-	-	-	

Possible contamination sources: P = pipework and/or borehole casing F = suspended material where low flow or the pipe-work arrangement precluded on-site filtration.

Table 5.1A

The remaining twelve determinands were undetected in the majority of the groundwaters. The ICP-OES detection limits (allowing for 20-times concentration of the samples) are presented below, with the few samples in which the elements were detected. Concentrations are in $\mu g\ l^{-1}$.

Element	Detection Limit ($\mu g\ l^{-1}$)
Al	5
Be	0.05
Cd	1.2
Co	0.8
Cr	1
La	1
Mo	2
Ni	1
Pb	10
Sc	0.05
Y	0.05
Zr	0.5

Al: site 3 (Car Dyke) -16
site 6 (Klondyke Stud Farm) - 21
site 16 (Mornington House Farm) - 29
site 26 (Forty Foot Farm) - 21
site 48 (Crowland Bridge) - 111
site 49 (Moulton West Fen) - 21

Be: site 9 (Northorpe Fen) - 1.3

Mo: site 26 (Black Hole Drove) - 3

Pb: site 1 (Billingborough New Inn House) - 27

Zr: site 29 (Deeping Fen Farm) - 0.5

Table 5.2A GROUNDWATERS - MARCH 1985

Site No.	Location	Grid reference	Date of sampling	Usage
3	Car Dyke Fm	5125132794	090385	P.S.
19	Twenty, Stables	5144032039	060385	P.S.
22	Daniel's, Quad Hi Fen	5198833152	070385	P.S.
23	Vicarage Fm	5176132817	090385	P.S.
24	Rigbolt House	5194732826	090385	over-flowing
25	Black Hole Drove	5178232514	090385	P.S.
31	Sixscore Fm, Langtoft Fen	5166331415	050385	P.S.
32	Elm Fm, Langtoft Fen	5152031291	060385	P.S.
33	Gibbs Fm, Langtoft Fen	5142631281	060385	P.S.
34	Bicker, Golden Drove	5247233850	070385	obs.
35	Donington, Caythorpe Fm	5221133623	070385	obs.
36	Gosberton	5244433148	070385	obs.
37	Cheal Bridge	5226032936	070385	obs.
39	Surfleet	5247932798	060385	obs.
40	Pinchbeck West	5211132713	090385	obs.
41	Newlands, Tydd Lane	5221532425	090385	P.S.
42	Spalding Bulb Co	5233132192	080385	obs.
43	Horseshoe Bridge	5218432115	080385	obs.
44	Cuckoo Bridge	5201331969	080385	obs.
45	Deeping St Nicholas	5222931798	060385	obs.
46	Orchard Villa, Deep St Nick	5212531598	060385	P.S.
49	Moulton West Fen	5288631583	060385	obs.
51	Dowsby, Hall Fm	5109812908	080385	P.S.

Usage: P.S. = private supply (domestic and/or irrigation, watering livestock etc.), obs. = A.W. observation borehole only

Table 5.2A

Distance from outcrop	Temp. °C	pH	Eh mV	Dissolved Oxygen mg l^{-1}	SEC µS cm^{-1}	Site No.
18.2	7.5	7.05	-	-	810	3
21.9	7.2	7.20	-	-	710	19
26.8	11.6	7.40	+91	-	670	22
24.2	11.1	7.10	+125	-	610	23
26.0	12.2	7.60	+51	-	710	24
24.8	11.1	7.75	+16	-	1110	25
24.7	11.7	8.20	+75	-	1250	31
23.6	6.0	7.50	-	-	760	32
22.7	11.2	7.30	+140	-	805	33
29.9	8.3	8.40	-	-	6350	34
27.7	10.5	8.50	-110	-	2050	35
30.6	12.9	8.10	-60	-	3025	36
29.0	12.4	7.45	+50	-	900	37
31.3	12.4	8.75	+25	-	1400	39
27.9	10.6	8.00	+110	-	1380	40
29.1	7.2	7.45	+95	-	1600	41
30.4	12.0	8.80	-50	-	3300	42
29.3	11.9	7.90	+78	-	1250	43
27.8	11.1	8.10	-10	-	1350	44
30.1	12.2	9.25	-45	-	4000	45
29.3	-	8.30	-	-	3100	46
36.8	10.5	7.90	+55	-	9150	49
17.5	9.8	7.50	-	-	415	51

Distance from outcrop (km) is measured along a transect (fig 5.1)

Table 5.2A

units - mg l^{-1}

Site	Na	K	Ca	Mg	HCO_3	SO_4	Cl	NO_3-N	Si
3	18	2.8	145	8.7	284	126	27	<0.1	3.0
19	33	2.2	95	9.7	305	69	20	<0.1	3.4
22	79	1.8	50	16.2	333	37	34	<0.1	3.8
23	59	2.0	60	15.7	318	37	129	<0.1	3.7
24	109	2.4	35	18.0	351	31	31	<0.1	3.8
25	213	2.8	25	7.1	440	44	126	<0.1	3.5
31	286	2.7	7	5.9	427	38	195	<0.1	3.6
32	36	3.2	73	15.8	310	84	55	0.3	3.7
33	73	3.1	73	15.3	311	81	47	<0.1	3.8
34	1462	7.4	15	12.4	651	<1	1930	<0.1	3.8
35	444	3.1	9	6.7	472	<1	455	<0.1	2.8
36	673	4.3	8	6.7	526	<1	785	<0.1	3.4
37	167	2.6	20	14.2	384	26	92	<0.1	3.9
39	322	2.7	5	3.6	469	18	245	<0.1	3.7
40	435	3.2	15	10.1	450	35	436	<0.1	4.2
41	387	2.6	4	3.3	483	29	288	2.8	3.3
42	740	4.5	8	6.9	549	26	830	<0.1	2.8
43	270	2.8	16	6.9	405	31	197	<0.1	3.3
44	292	2.7	7	3.4	433	31	197	<0.1	3.6
45	919	5.6	6	5.7	597	18	1130	<0.1	3.1
46	697	3.9	7	5.2	526	37	810	<0.1	3.7
49	2060	12.2	43	34.6	438	117	3060	<0.1	2.9
51	18	2.8	45	7.4	100	58	30	0.1	2.0

Table 5.2A

units - $\mu g\ l^{-1}$

Sr	Ba	F	Br	I	Li	B	P	S	Site
464	21	-	69	-	<0.1	58	-	-	3
645	23	-	72	-	<0.1	89	-	-	19
1725	23	1000	105	-	5.9	301	-	-	22
1574	24	-	116	-	<0.1	237	-	-	23
2024	20	1300	210	-	14	521	-	-	24
721	16	-	510	-	21	1171	-	-	25
679	8	2500	1380	-	18	1271	-	-	31
1671	24	-	255	-	13	432	-	-	32
1450	24	-	176	-	13	390	-	-	33
1726	27	3050	7575	-	60	3359	-	-	34
812	8	3700	1900	-	19	1692	-	-	35
833	8	4250	3300	-	29	2088	-	-	36
1489	13	-	620	-	16	708	-	-	37
414	4	3400	9260	-	18	1453	-	-	39
1422	13	-	1050	-	17	1285	-	-	40
407	5	-	1194	-	19	1748	-	-	41
861	9	4600	3490	-	37	2632	-	-	42
767	9	2780	800	-	19	1253	-	-	43
384	3	3080	860	-	18	1346	-	-	44
755	7	3600	3930	-	41	2838	-	-	45
728	9	2950	3375	-	32	2220	-	-	46
4651	45	1784	13750	-	117	3394	-	-	49
272	13	-	145	-	<0.1	55	-	-	51

Table 5.2A

units - $\mu g\ l^{-1}$

Site	Fe	Mn	Cu	Zn	
3	710	5	<10	247	P
19	742	3	<10	309	F
22	162	<3	<10	43	
23	99	<3	<10	<20	
24	137	<3	<10	<20	
25	188	3	<10	61	
31	37	<3	<10	<20	
32	24	13	<10	<20	
33	256	<3	<10	<20	
34	1216	6	39	<20	F
35	1047	26	<10	<20	
36	922	6	<10	<20	P
37	105	<3	<10	<20	
39	45	<3	<10	<20	
40	135	<3	<10	<20	
41	214	<3	<10	<20	
42	424	14	<10	<20	
43	29	3	<00	<20	
44	82	<3	<10	<20	
45	222	4	<10	<20	
46	886	3	<10	<20	PF
49	355	13	<10	1234	
51	-	110	<10	<20	

Possible sources of contamination: borehole casing and/or domestic pipework (P), suspended material when low-flow or pipework arrangement precluded on-site filtration

Table 5.2A

No preconcentration of the samples was carried out prior to analysis therefore the remaining determinands were undetected in all but one of the groundwaters. The ICP-OES detection limits are presented below.

Element	Detection Limit ($\mu g\ l^{-1}$)
Al	100
Be	1
Cd	25
Co	20
Cr	30
La	20
Mo	40
Ni	100
Pb	200
Sc	2
V	20
Y	2
Zr	15

Al: site 33 (Gibbs Farm) - 282

Table 5.3A GROUNDWATERS - SEPTEMBER 1984

Site No.	Location	Grid reference	Date of sampling	Usage
22	Daniel's, Quad Hi Fen	5198833152	260984	P.S.
25	Black Hole Drove	5178232514	270984	P.S.
31	Sixscore Fm, Langtoft Fen	5166331415	250984	P.S.
33	Gibbs Fm, Langtoft Fen	5142631281	240984	P.S.
36	Gosberton	5244433148	260984	obs.
37	Cheal Bridge	5226032936	270984	obs.
38	Risegate, Gotobed's	5215632898	260984	P.S.
39	Surfleet	5247932798	260984	obs.
41	Newlands, Tydd Lane	5221532425	270984	P.S.
42	Spalding Bulb Co	5233132192	250984	obs.
44	Cuckoo Bridge	5201331969	250984	obs.
45	Deeping St Nicholas	5222931798	250984	obs.
46	Orchard Villa, Deep St Nick	5212531598	260984	P.S.
48	Crowland Bridge	5229831067	250984	obs.
49	Moulton West Fen	5288631583	250984	obs.
52	Bertie Fen Farm	5220032780	270984	P.S.

Usage: P.S. = private supply (domestic and/or irrigation, watering livestock etc.), obs. = A.W. observation borehole only

distance from outcrop	temp. °C	pH	Eh mV	dissolved oxygen mg l^{-1}	SEC µS cm^{-1}	site No.
26.8	11.6	7.10	+106	-	430	22
24.8	11.1	7.75	+36	-	955	25
24.7	11.9	8.10	+41	-	1200	31
22.7	11.1	6.80	+171	-	745	33
30.6	12.6	8.15	-64	-	1200	36
29.0	11.6	7.65	+51	-	760	37
28.0	11.6	7.35	+11	-	610	38
31.3	11.5	8.10	+1	-	1200	39
29.1	12.5	8.10	+31	-	1500	41
30.4	12.8	8.80	-99	-	2475	42
27.8	12.3	8.55	+31	<0.2	1050	44
30.1	11.6	8.20	+76	-	3575	45
29.3	12.5	8.25	-49	-	3000	46
31.7	11.0	7.85	+136	-	5100	48
36.8	11.5	7.80	+71	<0.2	8070	49
17.5	-	7.85	-	-	657	52

Distance from outcrop (km) is measured along a transect (fig 5.1)

Table 5.3A

units - mg l^{-1}

Site	Na	K	Ca	Mg	HCO_3	SO_4	Cl	NO_3-N	Si
22	77	1.8	48	16	329	34	335	<0.1	3.3
25	208	2.4	24	6.6	414	46	106	<0.1	3.1
31	280	2.4	7.0	5.5	411	39	189	<0.1	3.2
33	109	2.9	64	14	341	84	62	<0.1	3.5
36	671	4.0	7.7	6.4	512	<1	805	<0.1	3.0
37	166	2.3	18	13	380	27	895	<0.1	3.5
38	107	2.0	35	15	376	31	49	<0.1	3.5
39	330	2.5	4.2	3.4	458	27	240	<0.1	3.0
41	378	2.5	4.0	3.2	476	32	302	<0.1	2.8
42	632	3.6	6.4	4.6	527	19	650	<0.1	1.6
44	289	2.4	6.3	3.1	437	31	192	<0.1	3.2
45	890	4.8	11	6.1	594	43	1080	<0.1	3.0
46	700	3.5	6.8	4.9	502	34	805	<0.1	2.9
48	1136	6.6	17	17	644	102	1500	<0.1	2.9
49	2093	11.6	50	34	463	119	3080	<0.1	2.8
52	148	2.2	24	14	391	30	69	<0.1	3.5

units - µg l^{-1}

Sr	Ba	Li	B	S	Fe	Site
1725	19	6.7	300	15	276	22
710	13	176	1140	2	1155	25
660	6	14	1260	9	47	31
1333	47	15	57	15	146	33
840	5	24	2150	2	1028	36
1400	10	12	710	4	127	37
1630	16	10	450	6	1887	38
420	2	15	1470	15	17	39
410	2	15	1800	4	254	41
640	4	27	2500	2	168	42
380	1	14	1350	4	61	44
930	5	34	2870	2	52	45
720	6	27	2260	3	664	46
2140	20	53	2420	19	94	48
5300	45	114	3440	-	423	49
1530	13	11	610	4	205	52

Table 5.3A

No preconcentration of the samples was carried out prior to analysis therefore the remaining elements were undetected in most of the groundwaters. The ICP-OES detection limits and samples in which the determinands were detected are presented below.

Element	Detection Limit ($\mu g\ l^{-1}$)
Al	100
Be	1
Cd	25
Co	20
Cu	10
Cr	30
La	20
Mo	40
Mn	3
Ni	100
Pb	200
Sc	2
V	20
Y	2
Zn	20
Zr	15

Al: site 33 (Gibbs Farm) - 152

Mn: site 33 (Gibbs Farm) - 5
site 46 (Orchard Villa) - 3
site 42 (Spalding Bulb Company) - 17
site 36 (Gosberton) - 4
site 49 (Moulton West Fen) - 9

Zn: site 25 (Black Hole Drove) - 45
site 22 (Daniel's, Quadring High Fen) - 50
site 52 (Bertie Fen Farm) - 108
site 41 (Newlands Farm) - 34
site 39 (Surfleet) - 11
site 48 (Crowland Bridge) - 693
site 49 (Moulton West Fen) - 121

F, Br, I and P not determined

GROUNDWATERS - MAY 1984 **Table 5.4A**

Site No.	Location	Grid reference	Date of sampling	Usage
36	Gosberton	5244433148	310584	obs.
42	Spalding Bulb Co	5233132192	310584	obs.
44	Cuckoo Bridge	5201331969	310584	obs.
43	Horseshoe Bridge	5218432115	310584	obs.
45	Deeping St Nicholas	5222931798	310584	obs.
48	Crowland Bridge	5229831067	300584	obs.
49	Moulton West Fen	5288631583	310584	obs.

all sites are A.W. observation boreholes

Distance from outcrop*	Temp. °C	pH	Eh mV	Dissolved Oxygen mg l^{-1}	SEC µS cm^{-1}	Site No.
30.6	13.0	8.3	-105	<0.2	2800	36
30.4	12.4	9.0	-149	<0.2	2600	42
29.3	12.9	8.0	-50	<0.2	1100	43
27.8	11.8	8.1	+4	<0.2	1150	44
30.1	12.1	9.1	-110	<0.2	2500	45
31.7	-	-	-419	-	-	48
36.8	10.0	9.4	-214	<0.2	8000	49

*Distance from outcrop (km) is measured along a transect (fig 5.1)

units - mg l^{-1}

Site	Na	K	Ca	Mg	HCO_3	SO_4	Cl	NO_3-N	Si
36	691	4.2	7.9	6.8	423	<1	208	<0.1	3.2
42	665	4.2	5.0	4.7	537	7	720	<0.1	1.5
43	283	2.8	16	1.3	423	33	208	<0.1	3.3
44	296	2.7	6.8	3.4	445	33	192	<0.1	3.3
45	926	5.9	5.5	5.4	597	16	1090	<0.1	2.0
48	1243	-	1.2	<1	-	44	1920	<0.1	-
49	2120	12.3	8.1	28	376	77	3100	<0.1	0.2

units - µg l^{-1}

Sr	Ba	Li	B	Fe	Site
808	7	28	2129	975	36
561	5	31	2515	141	42
739	9	19	1274	21	43
374	3	18	1354	81	44
699	6	39	2949	32	45
351	5	51	2548	11	48
1678	79	128	3178	80	49

Table 5.4A

The ICP-OES detection limits for the remaining elements and samples in which these determinands were detected are presented below.

Element	Detection Limit ($\mu g\ l^{-1}$)
Al	10
Cd	1
Co	1
Cu	1
Cr	1
La	1
Mo	5
Mn	3
Ni	3
Pb	20
Sc	2
V	1
Y	1
Zn	2
Zr	1

Al: site 44 (Cuckoo Bridge) - 24

Cd: site 49 (Moulton West Fen) - 5

La: site 49 (Moulton West Fen) - 4

Mo: site 49 (Moulton West Fen) - 28

Cu: site 44 (Cuckoo Bridge) - 8

F, Br, I and P - not determined